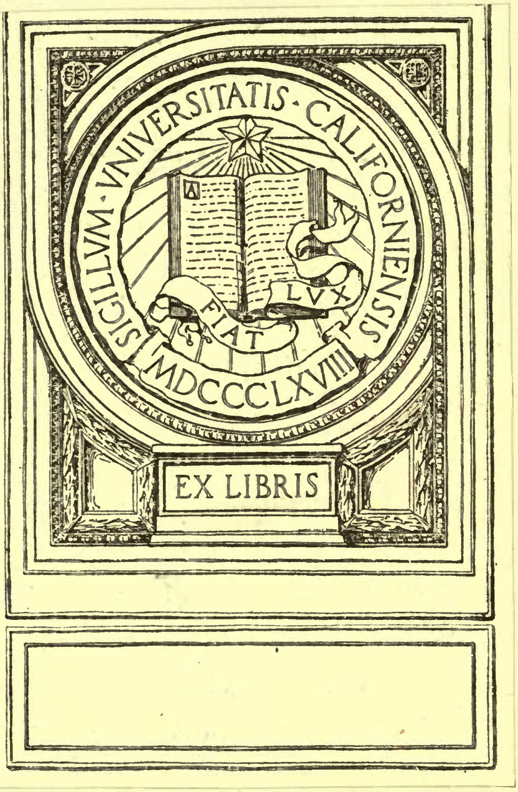

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A DICTIONARY
OF
APPLIED CHEMISTRY

VOL. IV.

A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

Assisted by Eminent Contributors

REVISED AND ENLARGED EDITION

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LONGMANS, GREEN, AND CO.

LONDON, NEW YORK, BOMBAY, AND CALCUTTA

A DICTIONARY
OF
APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

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IN FIVE VOLUMES

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WITH ILLUSTRATIONS

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1913

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A. I. L.

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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OILSTONE. A fine-grained hone-stone used with oil for sharpening edged tools. The most celebrated is the Turkey oilstone, an extremely hard and compact material, obtained in the interior of Asia Minor, and exported from Smyrna. It contains 70–75 p.c. silica, 20–25 p.c. calcium carbonate, and a little alumina. Two varieties are recognised, the white and the black, the latter being slightly the harder. In this country the Charley Forest stone has obtained great repute as an oilstone for whetting tools and penknives. It is a fine-grained, silicious, slaty rock, worked at Whittle Hill in Charnwood Forest, Leicestershire. The Welsh oilstone is a somewhat similar material, from near Llyn Idwal in North Wales, whilst the Devonshire oilstones are obtained from the neighbourhood of Tavistock. Several kinds of oilstone are worked in the United States. The Arkansas stone is a compact or fine-grained rock of bluish-white colour, used for delicate instruments, like those of surgeons and watchmakers. Somewhat similar, but more abundant, is the Washita oilstone, a white, opaque stone used chiefly by carpenters, from the Washita (or Ouachita) River, Arkansas. The name ‘novaculite’ is also applied to the Arkansas and Washita stones. Their material consists almost entirely of chalcedonic silica (99·5 p.c.).

In preparing oilstones for use, the rough pieces are cut into regular shapes on the lapidary’s wheel, fed with diamond powder, and are rubbed smooth with sand or emery on an iron plate. The slab of stone is in some cases cemented to a wooden base, by means of putty. Some of the stones are used not only for sharpening tools, but for finishing turned and planed surfaces of metal work. Oilstone powder is also employed for grinding the brass fittings of mathematical instruments (*v.* R. Knight, Trans. Soc. Arts, 50, 233; C. Holtzapffel, Turning, vol. 3, 1081; and G. P. Merrill, The Non-metallic Minerals, 2nd edit., 1910; *v.* also Whetstones).

F. W. R.

OKRA, also called gumbo; *Hibiscus esculentus* (Linn.), an annual plant bearing edible pods. Zega (Chem. Zeit. 1900, 24, 871) found as the average of 4 analyses—

Water	Protein	Fat	N-free extract	Fibre	Ash
80·7	4·2	0·4	12·1	1·2	1·4

According to American analyses (Bull. 28, U.S. Dept. of Agric. 1899), the edible portion of the pods, used largely as a vegetable in America, is much more watery, as shown by the following figures:—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
90·2	1·6	0·2	4·0	3·4	0·6

whilst, according to the same authority, canned okra contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
94·4	0·7	0·1	2·9	0·7	1·2

(*v.* also Tinsley, Amer. Chem. J. 1893, 14, 625).

H. I.

OLD FUSTIC is the wood of a tree known as the *Chlorophora tinctoria* (Gaudich), previously called *Morus tinctoria* (Linn.) which occurs wild in different tropical regions. The tree frequently grows to a height of over 60 feet, is exported in the form of logs, sawn straight at both ends, and usually deprived of the bark. The best qualities of old fustic come from Cuba and the poorer from Jamaica and Brazil. It is at the present time used very largely, and, together with logwood, is the most important of the natural dyestuffs.

The colouring matters of old fustic were first investigated by Chevreul (Leçons de chimie appliquée à la teinture, II. 150), who described two substances, one sparingly soluble in water, called *morin*, and a second somewhat more readily soluble. Wagner (J. pr. Chem. [i.] 51, 82) termed the latter *moritannic acid*, and considered that it possessed the same percentage composition as morin. Hlaziwetz and Pfaundler (Annalen, 127, 351), on the other hand, found that the so-called moritannic acid was not an acid, and as moreover its composition and properties were quite distinct from those of morin, they gave it the name ‘Maclurin.’

Morin $C_{15}H_{10}O_7,2H_2O$. To isolate this colouring matter from old fustic a boiling extract of the rasped wood is treated with a little acetic acid and then with lead acetate solution. This causes the precipitation of the morin in the form of its yellow lead compound, whereas the main bulk of the maclurin remains in solution. The washed precipitate in the form of a thin cream is run into boiling dilute sulphuric acid, and the hot liquid, after decantation from the lead sulphate, is allowed to stand. Crystals of crude morin are gradually deposited, and a further quantity can be isolated from the acid solution by means of ether. During the preparation of commercial fustic extract, the solution on standing, or the concentrated extract itself, deposits, as a rule, a brownish-yellow powder, which consists principally of a mixture of morin and its calcium salt, and this forms the best source for the preparation of large quantities of the colouring matter. The product is digested with a little boiling dilute hydrochloric acid to decompose the calcium compound, extracted with hot alcohol, and the extract evaporated. Crystals of morin separate on standing, and a further quantity can be isolated by the cautious addition of a little boiling water to the mixture.

Crude morin can be partially purified by crystallisation from dilute alcohol or dilute acetic acid, but the product usually contains a trace of maclurin. To remove the latter the finely powdered substance is treated in the presence of a little boiling acetic acid with fuming hydrobromic acid (or hydrochloric acid), which precipitates the morin as halogen salt, whereas the maclurin remains in solution (Bablich and Perkin, Chem. Soc. Trans. 1896, 69, 792). The crystals are collected, washed with acetic acid, decomposed by water, and the regenerated morin crystallised from dilute alcohol.

Morin crystallises in colourless needles (B. and P.), readily soluble in boiling alcohol, soluble in alkaline solutions with a yellow colour. Lead acetate solution gives a bright orange-coloured precipitate and ferric chloride an olive-green colouration.

Loewe (Zeitsch. anal. Chem. 14, 112) was the first to assign to morin the formula $C_{15}H_{10}O_7$, and that this was correct was shown by the analysis of its compounds with mineral acids (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 649). The *hydrochloride*, *hydrobromide*, and *hydriodide* are obtained in orange-coloured needles, and possess the formulæ $C_{15}H_{10}O_7{\cdot}HCl$, $C_{15}H_{10}O_7{\cdot}HBr$, and $C_{15}H_{10}O_7{\cdot}HI$, but the sulphuric acid compound, known as *anhydromorin sulphate* $C_{15}H_8O_6{\cdot}H_2SO_4$, orange-red needles, is of an abnormal character. *Monopotassium morin* $C_{15}H_9O_7K$, yellow needles, *monosodium morin* $C_{15}H_9O_7Na$, *magnesium morin* $(C_{15}H_9O_7)_2Mg$, orange-yellow needles, and *barium morin* $(C_{15}H_9O_7)_2Ba$, orange crystalline powder, have also been prepared (Perkin, Chem. Soc. Trans. 1899, 75, 437).

When an alcoholic solution of morin is treated with bromine (Benedikt and Hazura, Monatsh. 5, 667; Hlaziwetz and Pfaundler, J. 1864, 557) it is converted into *tetrabrom-morin ethyl ether* $C_{15}H_5Br_4O_7Et,2H_2O$, colourless needles, m.p. 155° (Herzig, Monatsh. 18, 700), and this when digested with stannous chloride and hydrochloric acid gives *tetrabromo-morin* $C_{15}H_6Br_4O_7$ (B. and H.), colourless needles, m.p. 258°. According to Perkin and Bablich, this latter compound is more simply prepared by the direct bromination of morin suspended in acetic acid.

Morin forms few crystalline derivatives. By the action of acetic anhydride, according to the usual methods, a colourless amorphous product results, and a crystalline pentacetylmorin has not yet been prepared. Cold acetic anhydride, however, converts the monopotassium salt of the colouring matter into *tetra-acetyl morin* $C_{15}H_6O_7(C_2H_3O)_4$, colourless prismatic needles, m.p. 142°–145°, but this on further acetylation gives an amorphous compound.

Tetrabromomorin, on the other hand, yields a *penta-acetyl derivative* (Bablich and Perkin) $C_{15}HBr_4O_7(C_2H_3O)_5$, colourless needles, 192°–194°, and it was subsequently found by Herzig that tetrabromomorin ethyl ether yields the compound $C_{15}HBr_4O_7Et(C_2H_3O)_4$, m.p. 116°–120°.

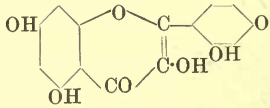
By fusion with alkali morin gives *phloroglucinol* (H. and P.), and *resorcinol* (B. and H.), whereas in this manner Bablich and Perkin isolated *β-resorcylic acid.* When methylated with methyl iodide *morin tetramethyl ether* $C_{15}H_6O_3(OCH_3)_4$ (B. and P.), yellow needles, m.p. 131°–132°, is produced, but is isolated with difficulty, and from this compound with alcoholic potash a yellow potassium salt, readily decomposed by water, is obtained. *Monoacetyltetramethylmorin* $C_{15}H_5O_3(OCH_3)_4C_2H_3O$, colourless needles, melts at 167°.

Morin tetraethyl ether $C_{15}H_6O_3(OC_2H_5)_4$ (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 61), yellow needles, m.p. 126°–128°, and *acetylmorintetraethyl ether*

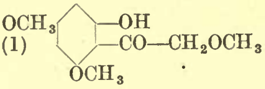
$$C_{15}H_5O_3(OC_2H_5)_4C_2H_3O,$$

colourless needles, m.p. 121°–123°, could only be prepared in small quantity.

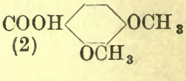
When *morin tetramethyl ether* is hydrolysed with alcoholic potash *β-resorcylic acid dimethyl ether*, and *phloroglucinolmonomethyl ether* are produced. Bablich and Perkin assigned to morin the constitution of a *pentahydroxyflavone* (tetrahydroxyflavonol)—



and that this formula correctly represents the substance, has been proved by its synthesis (Kostanecki, Lampe and Tambor, Ber. 1906, 39, 625), and also by the investigation of Herzig and Hofmann (Ber. 1909, 42, 155). It has been shown by the latter chemists that when morin is methylated by means of methyl sulphate *morin pentamethyl ether* $C_{15}H_5O_2(OCH_3)_5$, needles, m.p. 154°–157°, can be produced. This compound is hydrolysed with boiling alcoholic potash into *β-resorcylic acid dimethyl ether* (1), and *fisetol trimethyl ether* (1) (*cf.* QUERCETIN and FISETIN)—



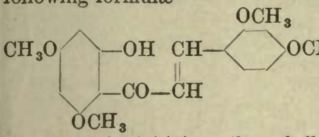
(1)



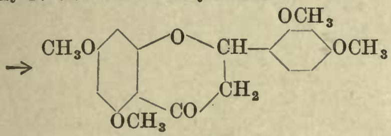
(2)

the latter being identical with the compound obtained in a similar way from quercetin pentamethyl ether.

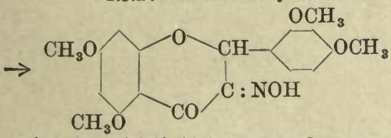
Kostanecki, Lampe and Tambor (Ber. 1906, 39, 625) have synthesised morin by reactions similar to those found serviceable in the artificial preparation of fisetin and quercetin (*see* YOUNG FUSTIC and QUERCITRON BARK), but in this case the formation of the flavanone did not proceed smoothly and only a small quantity could be prepared. The synthesis is illustrated by the following formulæ—



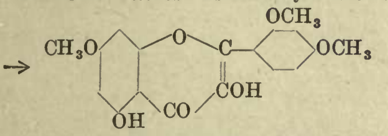
2′-hydroxy-4′:6′:2:4-tetramethoxychalkone.



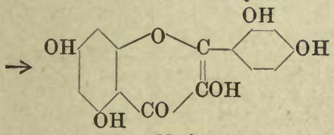
1:3:2′:4′-tetramethoxyflavanone.



a-isonitroso-1:3:2′:4′-tetramethoxyflavanone.



Morin trimethyl ether.



Morin.

Morin dyes mordanted woollen cloth shades which, though of a slightly stronger character, closely resemble those given by kaempferol.

	Chromium	*Aluminium*	*Tin*	*Iron*
Morin .	Olive yellow	Yellow	Lemon yellow	Deep olive brown
Kaempferol	Brown yellow	,,	Bright yellow	Deep olive brown

(Perkin and Wilkinson, Chem. Soc. Trans. 1902, 81, 590).

Maclurin $C_{13}H_{10}O_6$. When morin is precipitated from a hot aqueous extract of old fustic by means of lead acetate the solution contains maclurin. After removal of lead in the usual manner, the liquid is partially evaporated and extracted with ethyl acetate, which dissolves the colouring matter. The crude product is crystallised from dilute acetic acid (Perkin and Cope). A crude maclurin is also obtained during the preparation of fustic extract, partially in the form of its calcium salt, and this product is treated with dilute hydrochloric acid and crystallised from water. In order to decolourise the crystals, acetic acid is added to a hot aqueous solution and a little lead acetate in such quantity that no precipitate is formed, and the solution is treated with sulphuretted hydrogen. The clear liquid is now much less strongly coloured, and after repeating the operation two or three times, the maclurin, which crystallises out on standing, possesses only a pale yellow tint.

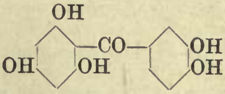
When quite pure maclurin consists of colourless needles, m.p. 200° (Wagner, J. 1850, 529), somewhat soluble in boiling water, soluble in alkalis with a pale yellow colouration. With aqueous lead acetate it gives a yellow precipitate and with ferric chloride a greenish-black colouration.

Hlasiwetz and Pfaundler (J. 1864, 558) assigned the formula $C_{13}H_{10}O_6$ to maclurin, and found that by boiling with potassium hydroxide solution it gives *phloroglucinol* and *protocatechuic acid.*

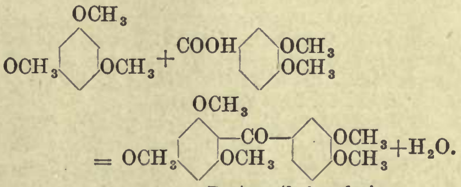
Pentabenzoylmaclurin $C_{13}H_5O_6(C_7H_5O)_5$ melts at 155°–156° (König and Kostanecki, Ber. 1894, 27, 1996); and *tribrom maclurin*

$$C_{13}H_7Br_3O_6,H_2O,$$

colourless needles has been obtained by Benedikt. *Maclurin pentamethyl ether* $C_{13}H_5O(OCH_3)_5$, colourless leaflets, melts at 157°. König and Kostanecki first assigned to maclurin the constitution of a *pentahydroxybenzophenone*—

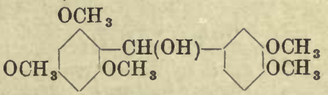


W. H. Perkin and Robinson (Chem. Soc. Proc. 1906, 22, 305), and somewhat later Kostanecki and Tambor (Ber. 1906, 39, 4022) synthesised maclurin pentamethyl ether, by the interaction of veratric acid and phloroglucinol trimethyl ether in presence of aluminium chloride—



Pentamethylmaclurin.

When maclurin pentamethyl ether is digested with alcoholic potash and zinc-dust *leucomaclurin-pentamethyl ether* (Kostanecki and Lampe, Ber. 1906, 39, 4014)



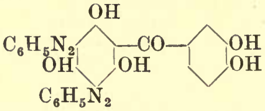
is produced in prismatic needles, m.p. 109°–110°, and this on further reduction gives *pentamethoxydiphenyl methane*, m.p. 107°–108°.

On the other hand, if leucomaclurin pentamethyl ether is oxidised in acetic acid solution, *veratric acid* and *dimethoxybenzoquinone* are formed.

Maclurin is interesting as it represents the only simple benzophenone colouring matter which is as yet known to exist in nature. It is possible, however, that kinoin from Malabar kino, and aromadendrin from eucalyptus kino also belong to this class (*v.* KINO).

Patent fustin. Under the name of ‘patent fustin’ a colouring matter has been placed on the market, which consists chiefly of disazobenzene maclurin (C. S. Bedford, 1887; Eng. Pat. 12667). To prepare this substance old fustic is extracted with boiling water, the solution is decanted from the precipitate of morin and its calcium salt which separates on cooling, and is neutralised with the necessary quantity of sodium carbonate. Diazobenzene sulphate is then added until a precipitate no longer forms, and this is collected and washed with water. It is sold in the form of a paste and dyes chrome mordanted wool an orange-brown shade.

Disazobenzene maclurin (Bedford and Perkin, Chem. Soc. Trans. 1895, 67, 933; *ibid.* 1897, 71, 186) which crystallises in salmon-red prismatic needles, m.p. 270° (decomp.) has the following constitution—



With acetic anhydride it gives *triacetyl disazobenzene maclurin* $C_{13}H_5O_5(C_6H_5N_2)_2(C_2H_3O)_3$, in orange-red needles, m.p. 240°–243° (decomp.).

Dyeing properties of old fustic. In silk and cotton dyeing fustic is employed to a comparatively limited extent, but in wool dyeing it is the most important natural yellow dyestuff. The olive-yellow or old gold colours which fustic yields when used with chromium mordant and the greenish olives obtained with the use of copper and iron mordants are all fast to light and milling, but the yellow colours yielded in conjunction with aluminium and tin possess only a moderate degree of fastness with respect to light. Fustic is chiefly employed in wool dyeing with potassium dichromate as the mordant, and it is for the most part used along with other dyestuffs, *e.g.* logwood, alizarin, &c., for the production of various compound colours, olive, brown, drab, &c. A. G. P.

OLEFIANT GAS *v.* Ethyl.

OLEFINES. Hydrocarbons of the C_nH_{2n} series homologous with ethylene.

OLEIC ACID *v.* Oils, Fixed, and Fats; Saponification.

OLEIN *v.* Oils, Fixed, and Fats; Glycerin.

OLEOMARGARINE *v.* Margarine.

OLEO-RESINS. Under the generic term oleo-resins are here described the chief representatives of that large group of natural products the essential constituents of which are resin and volatile oil. These substances are, for the most part, the oleo-resinous juices of plants more or less deprived of their volatile oil by evaporation, but still retaining enough for it to rank as one of their two leading components. For a more detailed list of oleo-resins, the numerous reports on botanical economics, and the catalogues of the various museums, should be consulted. Compare also the introduction to the article on Resins.

Copaiba. *Oleo-resin copaiba*; *Balsam of copaiba or copaiva or capivi*; (*Baume ou oléo-résine de copahu*, Fr.; *Copaiva balsam*, Ger.). Copaiba is the oleo-resinous secretion of the trees of the genus *Copaifera*, especially the species *C. Lansdorfii* (Desf.), which inhabit the warmer districts of South America. Descriptions of the leading species yielding the so-called balsam are given by Flückiger and Hanbury (Flück. a. Hanb. 227) and Bentl. a. Trim. 93. The drug became known in Europe in the seventeenth century, and was included in the Amsterdam Pharmacopœia of 1636 and the London Pharmacopœia of 1677. The yield of oleo-resin from a single tree is very great, the ducts containing it distending sometimes to such an extent as to burst the unyielding trunk with a report which is heard at long distances. In commerce the Pará variety is distinguished from that coming from Maranham and from the rarer Maracaibo copaiba.

In trade the oleo-resin occurs as a transparent, rarely opalescent, viscid liquid of a pale-yellow or light golden-brown colour, and a characteristic aromatic, not disagreeable, odour and persistent acrid bitterish taste. The specific gravity, which varies with the proportion of oil present, is generally 0·94 to 0·993. Alcohol, benzene, carbon disulphide, or acetone dissolve most specimens of copaiba: glacial acetic acid dissolves the resin only. When mixed with small quantities of magnesia, lime, or baryta, most specimens form a stiff mixture which gradually hardens. This depends upon the presence of an acid resin which forms solid combinations with alkaline earth metals. Flückiger (Jahresb. Pharm. 1867, 162; 1868, 140) finds the action of copaiba on polarised light to vary, some specimens being dextro- and others lævorotatory.

The *volatile oil* in copaiba varies from 20 to 80 p.c., the percentage of *resins*, which are the sole other constituents, showing corresponding differences. A method for the estimation of the volatile oil is given by Cripps (Pharm. J. [iii.] 22, 193).

Volatile oil of copaiba or *copaivene* $C_{20}H_{32}$ is an isomeride of oil of turpentine. It boils at 252°–256°, is soluble in 8 to 30 parts of alcohol (sp.gr. 0·830), or in 3 parts of absolute alcohol, and has a sp.gr. of 0·88 to 0·91. The oil has the odour and taste of copaiba. When hydrogen chloride is passed into the dried oil, crystals of *copaivene hydrochloride* $C_{20}H_{32},4HCl$ are formed (Levy and Engländer, Annalen, 242, 191). *Cf.* Bonastre (J. Pharm. 11, 529); Ader (*ibid.* 15, 95); Gerber (Br. Arch. 30, 157); Blanchet (Annalen, 7, 156); Soubeiran and Capitaine (J. Pharm. 26, 70); Aubergier (*ibid.* 27, 278); Gerhardt (Compt. rend. 17, 314); Chautard (*ibid.* 34, 485); and Posselt (Annalen, 69, 67). The terpene of Maracaibo copaiba boils at 250°–260°, and gives no crystalline hydrochloride (Brix, Monatsh. 2, 507). A dark-blue *hydrate* $(C_{20}H_{32})_3,H_2O$ is obtained towards the end of the operation when the moist terpene is distilled over sodium (Brix).

The oil from copaiba balsam collected in Surinam from *Copaifera guyanensis* (Desf.) boils, for the most part, at 254°–262°, and appears to be a mixture of two *sesquiterpenes*. The fraction boiling at 270°–280° contains a little cadinene. Towards the end of the steam distillation of the balsam, a *sesquiterpene alcohol* $C_{15}H_{26}O$, m.p. 114°–115°, separates in the condenser from which a *sesquiterpene* $C_{15}H_{24}$, b.p. 252°, is obtained. The latter is a mobile liquid which soon changes in the air to a resinous solid (van Itallie and Nieuwland, Arch. Pharm. 242, 539; 244, 161).

Of the copaiba resins many are found only in certain varieties of the oleo-resin. The most important is the crystalline acid resin *copaivic acid* $C_{20}H_{30}O_2$. This constitutes by far the greater portion of the crude resin, and may be obtained according to Schweitzer (Pogg. Ann. 17, 784; 21, 172) by dissolving the resins in aqueous ammonia and setting aside at a temperature of $-10°$, when it separates in the form of crystals. Copaivic acid was further studied by Rose (Pogg. Ann. 33, 83; Annalen, 13, 177; 40, 310) and Hess (*ibid.* 29, 140) when the formula was established. The acid is an isomeride of abietic acid. Crystalline deposits sometimes occur in copaiba. One of these, in an old specimen of the Trinidad variety, which was supposed to be copaivic acid, was examined by Flückiger and Hanbury (Flück. a. Hanb. 231). It melted at 116°–117°. Another deposit investigated by Fehling (Annalen, 40, 110) proved to be an allied compound *oxycopaivic acid* $C_{20}H_{28}O_3$. Similarly, Strauss (*ibid.* 148, 148) extracted *metacopaivic acid* $C_{22}H_{34}O_4$ from Maracaibo copaiba. Copaiba from Maracaibo and Pará has been examined by Tschirch and Keto (Arch. Pharm. 239, 548). After separation of the resin acids and the essential oil, a small quantity of a mixture of indifferent *resenes* remained mostly, but not wholly, soluble in alcohol. From the Para balsam, *paracopaivic acid* $C_{20}H_{32}O_3$, m.p. 145°–148°, extracted by 5 p.c. ammonium carbonate solution, and *homo-paracopaivic* acid $C_{18}H_{28}O_3$, m.p. 111°–112°, were obtained. From samples of Maracaibo copaiba, *β-metacopaivic acid* $C_{11}H_{16}O_2$ (or $C_{16}H_{24}O_3$), melting at 89°–90°, and *illuric acid* $C_{20}H_{28}O_3$, melting at 128°–129°, were isolated. Other resins have been described by Martin and Vigne (J. Pharm. Chim. [iii.] 1, 52), Posselt (Annalen, 69, 67), and Rush (Amer. J. Pharm. [iv.], 9, 305). *Cf.* Oberdöfer (Arch. Pharm. [ii.] 44, 172); Ulek (*ibid.* 122, 14); Procter (Pharm. J. [iii.] 10, 603); Roussin (J. Pharm. Chim. [iv.] 1, 321); Levy (Ber. 18, 3206).

Illurin oleo-resin, an African variety of copaiba, obtained from *Hardwickia Mannii* (Oliver) in the Niger basin, also examined by Tschirch and Keto, contains *illuric acid* which closely resembles Fehling's oxycopaivic acid. It crystallises in the hexagonal system and is a monobasic acid. It gives the cholesterol reactions and is not affected by fusion with potassium hydroxide; in these and other respects, it resembles the resin acids of the coniferæ, especially pimaric acid, but it differs from them by reducing silver salts in ammoniacal solution.

In medicine, copaiba is employed for its stimulating action on mucous membranes, especially those of the genito-urinary system.

Adulteration of copaiba has been largely practised. Turpentine, castor oil, and gurjun 'balsam' are typical of the adulterants employed. Numerous methods of testing have been proposed. These are reviewed by Siebold (Pharm. J. [iii.] 8, 251). It is shown that the specific gravity or percentage of resin and oil is so variable as to be of no value in detecting adulteration. Many properties while appertaining to most specimens of the oleo-resin are not found in all. Thus fluorescence, a character of gurjun 'balsam,' is not absent from all specimens of true copaiba; all specimens do not dissolve one-fourth of their weight of magnesium carbonate or form a clear solution with aqueous ammonia or alcohol. Benzene is a universal solvent for copaiba, but it behaves in the same manner toward all the ordinary adulterants. Muter (Analyst, 1, 160) devised a method for the 'detection of castor oil and other fats,' depending upon the separation of their sodium salts, but Siebold considers the following simpler method much more delicate. A gram or so is heated in a watch-glass until all oil is driven off, which is the case as soon as the residue assumes a rich-brown colour. If the remaining resin is brittle and pulverisable, no fatty oil is present. As little as 1 p.c. of oil can be thus detected. Gurjun or wood oil may be discovered by Flückiger's process (Flück. a. Hanb. 233 note). One drop of copaiba is agitated in a test tube with 19 drops of carbon disulphide, and to this is added a drop of a mixture of equal volumes of strong sulphuric and nitric (1·42) acids. After a little agitation, copaiba becomes reddish-brown with a deposit of resin on the sides of the tube; gurjun oil gives an intense purplish-red colour changing to violet, whilst the oleo-resin of *Hardwickia*, sometimes an adulterant of copaiba, gives no perceptible alteration of colour. By this procedure, 1 part of gurjun oil in 8 parts of copaiba may be detected. Another method is that of Hager (Pharm. Centh. 16, 257). 1 volume of copaiba mixed with 4 volumes of light petroleum gives either a clear solution or only a slight turbidity which, when it settles, forms not more than a thin film covering the bottom of the vessel. Gurjun oil is insoluble in light petroleum and settles in half an hour. Benzene cannot be substituted, as has been proposed, for light petroleum. Gurjun balsam can also be detected in copaiba by giving a reddish colouration, changing to blue, when the sample is boiled with 3 parts of 95 p.c. alcohol and 1 part of crystallised stannous chloride, and by affording a reddish or purple colour when 4 drops of copaiba are carefully added to a mixture of half an ounce glacial acetic acid with 4 drops of nitric acid (*cf.* Brit. Pharm.). The presence of oil of turpentine is recognised by Siebold during the evaporation for the detection of fixed oils, and may be further identified by distillation and fractionation of the volatile oil. Turpentine boils at 160°–180°, oil of copaiba at 240°–250°. See further: Bowman (Amer. J. Pharm. [iv.] 7, 385); Fulton (*ibid.* [iv.] 7, 550); Rush (Pharm. J. [iii.] 10, 5); Hager (Pharm. Centh. 1870, 296; 24, 141); Prael (Arch. Pharm. [iii.] 23, 735, 769); Wayne (Amer. J. Pharm. [iv.] 3, 326); Maupy (Chem. Zentr. 1894, i. 929); Hirschsohn (*ibid.* 1895, ii. 694).

Elemi. *Oleo-resina elemi* (*Résine elémi*, Fr.; *Elemiharz*, Ger.). The Greek and Roman writers describe a 'gum of Ethiopian olive' which has been generally identified with elemi. According to Flückiger and Hanbury (Flück. a. Hanb. 147), however, this ancient elemi is the oleo-resin known as *Luban meyeti.* Pliny terms the drug *enhæmon* or *enhæmi*, from which the name *animi* and perhaps also *elemi* is derived. The term 'animi' is also used for a kind of copal.

During the sixteenth century, the older African elemi was replaced by a drug of similar appearance, which came from Mexico, and South America, and this in its turn has given way to a product of the Philippine Islands, which is now the elemi of commerce.

Elemi or Animi of the older Writers; Oriental or African Elemi; Luban Meyeti; Luban Mati.

This drug is derived from *Boswellia Frereana* (Birdwood), a tree belonging to the same genus which yields the gum-resin olibanum, and which inhabits the hills immediately west of Cape Gardafui. Notwithstanding the close botanical relation to olibanum, and the generic name, Luban being Arabic for that drug, there is no doubt, owing to the entire absence of gum and other characters, that Luban Meyeti is a distinct product. According to Hanbury and Flückiger (Pharm. J. [iii.] 8, 805; Flück. a. Hanb. 147), this was the elemi of commerce until its place was taken, in the sixteenth century, by a somewhat similar product of Mexico and South America.

Luban elemi is described by Flückiger and Hanbury as detached droppy tears and fragments, occasionally in stalactitic masses several ounces in weight. Externally it has a thin-opaque white crust, but internally it is transparent and of an amber colour. It has an agreeable odour of lemon and turpentine, and a mild terebinthinous taste. The *volatile oil*, which has a fragrant elemi odour, from the specimen examined, amounted to 3·1 p.c. It has a specific gravity of 0·856 at 17°, and rotates the polarised ray slightly to the left. It consists partly of a dextrorotatory *hydrocarbon* $C_{10}H_{16}$, and partly of a lævorotatory *oxygenated oil*. The *resin* is mostly soluble in alcohol, and has the composition $C_{20}H_{30}O_2$.

Elemi of the Seventeenth and Eighteenth Centuries; American or Brazilian Elemi.

The oleo-resin, which replaced the older African elemi for the most part during the seventeenth and eighteenth centuries, was the product of several Brazilian trees, species of the genus *Protium* (*Icica*). A specimen examined by Flückiger and Hanbury (Flück. a. Hanb. 152), was a translucent greenish-yellow fragrant terebinthinous resin, which by means of cold spirits of wine could be separated into two portions—the one soluble, and the other, consisting of a mass of acicular crystals, insoluble. Scribe (Ann. Chim. Phys. [iii.] 13, 166) investigated one of the *Icica* oleo-resins which had lost all its volatile oil, and consisted of three neutral compounds, which he separated by the difference of their solubility in alcohol. From the alcoholic solution, *brean* first comes out in white pearly stellate needles, melting at 157°. Brean has the composition C 83·92 p.c., H 11·82 p.c., and O 4·26 p.c. In sulphuric acid it dissolves with a red colour. Further concentration of the alcoholic solution yields crystals of *icican*, which contain C 82·01 p.c., H 11·64, and O 6·35 p.c. From the mother-liquor a small quantity of an amorphous resin, *colophon*, was obtained.

The oleo-resin of *Protium heptaphyllum* (March.), was examined by Stenhouse and Groves (Chem. Soc. Trans. 29, 175). This is known as *Gum Hyawa*, or *Conima resin*, or *resin of the incense-tree*. It possesses a fragrant balsamic odour, which depends on the presence of a small proportion of *volatile oil*. This oil, when obtained by distillation with steam, boils at about 270°. By treatment with sodium and fractional distillation, it gives a hydrocarbon *conimene*, $C_{15}H_{24}$, which boils at 264°. If the residue, after removal of the volatile oil, be dissolved in hot alcohol, it deposits on cooling a crystalline compound, *icacin*, $C_{46}H_{76}O$, and the mother-liquor contains a yellow *amorphous resin*. Icacin melts at 175° (*cf.* Hesse Annalen, 192, 181). A comparison of the analytical numbers, melting-points, and other characters, points to the probability that while the icican of Scribe is only an impure form of that observer's brean, this, in its turn, is the icacin of Stenhouse and Groves in an imperfect condition of purity. The amorphous resin of the latter observers is also probably the colophon of Scribe. At all events, the evidence of the existence of brean and icican needs revision.

Elemi of Commerce of the Present Day; Manilla Elemi; Arbol a Brea Resin.

The tree which yields the elemi of the present day is a native of the Philippine Islands, and is called by the Spaniards *Arbol a brea*. Its botanical relations were not known until quite recently, but it is now certain that the oleo-resin is collected from *Canarium luzonicum* (Miq.), (Clover, Philippine J. Sci., 1907, 2, 2). Manilla elemi is a soft oleo-resin which, in appearance, resembles old honey. It occurs in commerce generally admixed with earthy or carbonaceous matter, which gives it a dark colour. When fresh and pure, it is colourless and has a fragrant odour. Cold spirits of wine applied to the drug discloses numerous acicular crystals visible under a microscope (Flück. a. Hanb.).

Elemi is a mixture of *volatile oil* and *resin*. The volatile oil contains *d*-phellandrene, dipentene, and a crystalline compound which may be identical with amyrin (Wallach, Annalen, 252, 102). Phellandrene and dipentene are also obtained by the dry distillation of the resin (Wallach, *ibid.* 271, 310).

The resin of elemi was first examined by Maujean (J. Pharm. 9, 45), who showed that it contains two resins, one soluble in cold and the other in hot alcohol. *Cf.* Rose (Annalen, 13, 192; 32, 297; 40, 307) and Hesse (*ibid.* 29, 136). Bonastre (J. Pharm. 10, 199) found the former to exist to the extent of 61 p.c., and the latter, which crystallised easily, 25 p.c. Baup (Ann. Chim. Phys. [iii.] 31, 108) called the latter *amyrin*. It is insoluble in water, readily soluble in ether and hot alcohol, and crystallises in satiny fibres, which melt at 174° (Baup) or 177° (Flück. a. Hanb.). *Cf.* Buri (Neues Rep. Pharm. 25, 193) and Hesse (Annalen, 192, 180). Amyrin, $C_{30}H_{50}O$, has been converted by Vesterberg into two crystalline isomeric acetates, $C_{30}H_{49}(C_2H_3O_2)$ and benzoates, $C_{30}H_{49}(C_7H_5O_2)$, from which two corresponding amyrins have been prepared. *α-Amyrin* melts at 181°–181·5°, (*α*)-*amyrin acetate* at 220° and *benzoate* at 192°; while *β-amyrin* melts at 193°–194°, (*β*)-*amyrin acetate* at 235°, and *benzoate* at 230° (Ber. 20, 1243; 23, 3186). Ciamician (Ber. 11, 1347), by distilling amyrin with zinc-dust, obtained toluene, methylethylbenzene, and ethylnaphthalene.

The alcoholic mother-liquor contains the *amorphous resin*, or resin soluble in cold alcohol, which is the largest constituent of elemi. Besides amyrin, Baup describes three other compounds occurring in elemi—*breïdin*, *breïn*, and *bryoïdin*. Breïn is certainly, in view of Flückiger and Hanbury's investigation, impure amyrin (*cf.* Vesterberg, Ber. 39, 2467), and the existence of breïdin requires further proof.

Specimens of Manila elemi have been examined by Tschirch and Cremer (Arch. Pharm. 240, 293). 100 parts of the drug contain: *manamyrin*, consisting of α and β amyrin, 20–25; essential oil, 20–25; *bryoïdin*, 0·8–1; *α-manelemic acid*, 5–6; *β-manelemic acid*, 8–10; *maneleresene*, 30–35; inorganic constituents and bitter substance, 1–2; impurities, 5–6 parts. Bryoïdin, $C_{21}H_{42}O_3$, m.p. 135·5°, was prepared by digesting the elemi with dilute alcohol at a gentle heat and evaporating the extract to crystallisation. It is neutral, has a bitter taste, and, whilst insoluble in cold water, dissolves readily in hot water and in alcohol and ether (Pharm. J. [iii.] 5, 142). α-Manelemic acid $C_{37}H_{56}O_4$, m.p. 215°, previously isolated by Buri (Pharm. J. [iii.] 8, 601), crystallises from the alcoholic solution of the acids, extracted from the resin by aqueous potassium carbonate, while the mother liquor contains amorphous β-manelemic acid $C_{44}H_{80}O_4$, m.p. 75°–76°. Maneleresene $C_{15}H_{30}O$ remains after the removal of the other constituents of the oleo-resin; it is amorphous and melts at 63°–65°.

Elemi is seldom used in medicine in this country. It is, however, sometimes employed in the form of ointment as a dressing for indolent ulcers. At present its chief use is in the preparation of printing inks, and occasionally as an ingredient in varnishes.

Oleo-resins allied to Elemi.

Anime. Much confusion exists as to the use of the word anime, and the same may be remarked of tacamahac. By some writers anime is used as synonymous with elemi, and by others it is restricted chiefly to a variety of copal. There are, however, a number of other oleoresinous products which are usually known as anime. The chief members of this class are:—1. *Gomart oleoresin*, or *gommier resin*, the exudation of *Dacorydes hexandra* (Griseb.), an inhabitant of the West Indies (Imp. Inst. Rep. No. 63, 192). This has an odour between that of elemi and turpentine. Owing to its general resemblance to true elemi, gommier resin is commonly known as 'dry' or West Indian elemi. For analysis and commercial valuation, see Imp. Inst. Report. The oleo-resin has been examined by More (Chem. Soc. Trans. 75, 718). The essential oil was found to contain 64 p.c. of *l*-pinene and 17 p.c. of sylvestrene, and from the resin a crystalline compound, m.p. 166°–167°, was obtained, having the composition $C_{25}H_{44}O$. 2. *Brazilian anime*, the product of *Hymenœa Courbaril* (Linn.), a tree belonging to the natural order *Leguminosœ*. The oleo-resin resembles mastic. It softens in the mouth, and when warmed emits a peculiar odour. The volatile oil is colourless, with a strong, not unpleasant odour and burning taste. It is completely soluble in alcohol (Paoli, Brugn. Giorn. 16, 326). After removal of the oil, cold alcohol extracts an *amorphous resin*, and the residue, dissolved in boiling alcohol, deposits on cooling a *semi-crystalline compound*, which was analysed by Laurent (Ann. Chim. Phys. [ii.] 66, 314). See also Batka (Pharm. J. [iii.] 6, 742); Guibourt (Rév. scient. 16, 177); Filhol (J. Pharm. Chim. [iii.] 1, 301, 507); Hancock (Ed. N. J. Sc. 1, 240); Manzini (J. Pharm. 27, 752); Deville (Annalen, 71, 354).

Carana. A soft oleo-resin allied to Brazilian elemi, probably derived from *Protium Carana* (March.) and allied species. It has a fragrant balsamic odour and somewhat bitter taste. It contains 96 p.c. of resin, soluble in alcohol (Pelletier, Bull. Pharm. 4, 241). Carana elemi from *Protium Carana* (March.), has been examined by Tschirch and Saal (Arch. Pharm. 241, 149), who found that in 100 parts of the drug there were contained iso*careleminic acid*, 2; *careleminic acid*, 8; *carelemic acid*, 10; essential oil, 10; amyrins, 20–25; resene, 30–35; impurities, 12–15 parts. For analytical constants *v.* Dieterich (Pharm. Centh. 40, 453).

Ceradia. The product of *Ceradia* (*Othonna*) *furcata* (Lindl.). It is an amber-coloured oleoresin with the odour of elemi (R. Thomson, Phil. Mag. 28, 422).

Mauritius elemi. An oleo-resin very closely resembling Manilla elemi. It is the yield of the *Canarium mauritianum* (Blume; Flück. a. Hanb. 152). It has been examined by Tschirch and Saal (Arch. Pharm. 242, 348). 100 parts of the drug were found to contain α-iso*colelemic acid*, 10; *coleleminic acid*, 2; β-iso*colelemic acid*, 8; *colamyrin*, 25–30; *coleresene*, 30–35; essential oil, 3; bitter principle and bryoïdin, plant remains and impurities, about 10 parts.

Mexican elemi. Vera Cruz elemi. Mexican elemi is not now an article of commerce. It is nearly related to Brazilian elemi. It is the reputed product of *Amyris Plumieri* (DC.); (Flück. a. Hanb. 152). This elemi has been examined by Tschirch and Cremer (Arch. Pharm. 240, 293), who find that it contains a very large proportion of substances which resist the action of alkalis (resene and amyrin) and this would make it peculiarly suitable for the basis of a lacquer.

Tacamahac. The following are the more important oleo-resins which have been described as tacamahac:—1. *East Indian tacamahac*, the product of *Calophyllum Inophyllum* (Linn.), which inhabits Bourbon and Madagascar. It is a dark-green balsamic resin—sp.gr. 1·032; m.p. 75°. 2. *Yellow tacamahac*, the exudation of *Amyris tacamahac* (Batka). It was labelled *Tacamahaque vierge* by Des Marchais, *African incense* by Pereira, and *Bdellium d'Afrique* by Guibourt. It melts at 100°, exhaling an agreeable odour, and the resin remaining is partly soluble in alcohol. The part insoluble in alcohol consists of yellow crystals—*tacamahacin*. This substance is insoluble in ether, sparingly soluble in alcohol, and is unaffected by alkalis or nitric acid. Sulphuric acid dissolves it with a violet colour (Batka, Pharm. J. [iii.] 6, 742). Yellow tacamahac is often termed anime. 3. *Oleo-resin of Protium heptaphyllum* (Aub.). This has been already described under the name of *conima resin* (see *Elemi of the seventeenth and eighteenth centuries*). A number of samples of Tacamahaca resin have been examined by Tschirch and Saal (Arch. Pharm. 242, 365, 395) and analytical constants are given by Dieterich (Pharm. Centh., 40, 453).

Besides these, which Batka regards as true tacamahacs, the product of *Protium Obtusifolium* (March), the *Mauritius tacamahac*, and common *galipot* of *Pinus Pinaster* (Soland), the latter under the name of the *bitter tacamahac of trees*, have been described as varieties of that drug.

Gurjun oleo-resin. *Gurjun balsam; Wood oil; Oleo-resina dipterocarpi.* This oleo-resin resembles and is used as an adulterant and substitute for copaiba. It is obtained from Burma and the Straits, being the product of various species of *Dipterocarpus* (Flück. a. Hanb. 88). Gurjun oil must not be confounded with the fatty oil which is also known as wood oil, or *wood oil of China*, which is expressed from the seeds of the *Aleurites cordata* (Steud.), the well-known *Tung* tree of the Chinese.

Gurjun, or wood oil, resembles copaiba in appearance, with the exception of its fluorescence, a character rarely found in copaiba. When heated in a closed tube to 220° it becomes almost solid, whereas copaiba similarly heated does not lose its fluidity. For other distinguishing characters *v.* COPAIBA.

Wood oil was examined by Lowe (Pharm. J. 13, 65); Hanbury (*ibid.* 15, 321); Martius (Neues Rep. Pharm. 5, 100); Guibourt (*ibid.* 6, 97), and Hirschsohn (Pharm. J. [iii.] 10, 561). Werner (Zeitsch. Chem. 1862, 588) found it to consist of 20 p.c. of *volatile oil* $C_{20}H_{32}$, a polymeride of turpentine, and a residual *resin* which contained *gurjunic acid* $C_{44}H_{68}O_8$, a crystalline compound soluble in aqueous ammonia. Other observers have found different percentages of oil and resin, which are indeed variable. The volatile oil boils at 255°–260° (Flück. a. Hanb.), 255° (Werner), and its sp.gr. is 0·915 (Flück. a. Hanb.); 0·904 (Werner); 0·928 (De Vry, Pharm. J. [iii.] 16, 374). Amyl alcohol dissolves the volatile oil, but it is only sparingly soluble in ethyl alcohol, and glacial acetic acid. The hydrocarbon is coloured a magnificent blue by hydrochloric acid, but does not form a crystalline hydrochloride.

When the resin of wood oil is extracted by alcohol and aqueous solution of ammonia added, and the *amorphous resin* which separates collected, the solution contains *ammonium gurjunate* from which gurjunic acid is obtained as a precipitate on the addition of a mineral acid, and it may then be recrystallised from ether or alcohol. Werner found it to melt at 220°, and to boil with decomposition at 260°. Gurjunic acid is soluble in alcohol, benzene, and carbon disulphide. It may be regarded as tri-hydrated abietic acid thus:—$C_{44}H_{64}O_5,3H_2O$. This formula agrees equally well with Werner's data. It is probably identical with the meta-copaibic acid of Strauss (*v.* COPAIBA). A *compound*, $C_{20}H_{30}O_2$, yielding a diacetate is obtained from gurjun oleo-resin and enters commerce as 'copaivic acid.' It is crystalline, melts at 126°–129°, is soluble in alcohol and ether but insoluble in water and alkalis (Brix, Monatsh. 2, 516). The amorphous resin which constitutes the chief part of the resin of wood oil consists of *gurjoresene* $C_{17}H_{28}O_2$, m.p. 40°–43° (Tschirch and Weil, Arch. Pharm. 241, 372). The deposits, largely crystalline in character, which are found in various samples of gurjun balsam, consist of resin-alcohols or resin phenols, but are insoluble in alkalis, in these respects resembling amyrin.

In addition to its use as a substitute for copaiba, wood oil is employed in India as a natural varnish, especially for ships.

Labdanum; *Ladanum.* A sticky, black-brown, soft oleo-resin, derived from *Cistus polymorphus* (Willk.) and other species of *Cistus*, inhabiting the Grecian Archipelago and the shores of the Mediterranean (*cf.* Bentl. a. Trim. 24). It is a variable mixture of resin, volatile oil, gum, wax, and earthy and woody impurities. The odour is fragrant, and it has a bitter taste. Guibourt (Hist. Drogues, 3, 601), Pelletier (Bull. Pharm. 4, 503), Johnston (Phil. Trans. 1840, 344), Thiselton Dyer (Pharm. J. [iii.] 15, 301; 16, 385, 779). For analytical constants, *see* Dieterich (Pharm. Centh., 40, 453).

Lupulin. *Lupulinic glands; Lupulina* (*Lupuline*, Fr.; *Hopfendrüsen*, *Hopfenstaub*, Ger.). The detached minute glands of the strobile of *Humulus Lupulus* (Linn.) contain *volatile oil*, a *bitter acid*, *resin*, *wax*, and possibly an *alkaloid.*

Commercial lupulin has been examined by Barth (Chem. Zentr. 1900, [ii.] 681), who found it to contain 18·27 p.c. of ash, 63·93 p.c. of material soluble in ether and 36·07 p.c. of lupulin husks. The portion soluble in ether contained 0·18 p.c. of wax, 11·55 p.c. of *α-resin*, 43·31 p.c. of *β-resin*, 0·17 p.c. of ash, and 8·72 p.c. of fat oil, *γ-resin*, &c. The proportion of sand in commercial lupulin varies from 10·9 to 20·2 p.c.

The volatile oil which exists to the extent of about 0·9 p.c. (Flück. a. Hanb. 553), consists according to Wagner (J. 1853, 516) and Personne (J. Pharm. Chim. [iii.] 26, 241, 321; 27, 22; J. 1854, 654) of a *terpene*, $C_{10}H_{16}$, boiling at 175°, and an oxygenated compound probably *valerol*, $C_6H_{10}O$, which boils at 210° and on oxidation yields *valeric acid.* The latter acid has also been detected in hops. The crude oil boils from 140°–300°. *Cf.* Mehu (Thèse, Montpellier, 1867), and Ossipow (J. pr. Chem. [ii.] 28, 448). Chapman (Chem. Soc. Trans. 67, 54, 780) finds that the oil can be separated into two fractions: one, boiling at 166°–171°, probably a mixture of two *hydrocarbons*, $C_{10}H_{16}$ and $C_{10}H_{18}$, and the other, a sesquiterpene, *humulene*, $C_{15}H_{24}$, b.p. 160°–170° (60 mm.). The latter gives a crystalline nitrosochloride, melting at 164°–165°.

The resins present in lupulin are divided into soft and hard resins, according as they are soluble or insoluble in light petroleum (Hayduck, Bied. Zentr. 1887, 694). The α-resin, a soft resin precipitated by lead acetate, contains *α-lupulinic acid*, which, when pure, is extremely resistant to chemical reagents but is rapidly transformed into a resin at a high temperature (Barth, Chem. Zentr. 1900, [ii.] 915; Siller, Zeitsch. Nahr. Genussm. 18, 241). The β-resin, which is also a soft resin, is not precipitated by lead acetate. It appears to be an oxidation product of an organic acid, *β-lupulinic acid*, first obtained from hops by Bungerer (Bull. Soc. chim. [ii.] 45, 489). To prepare lupulinic acid, lupulin is extracted with light petroleum and the crude crystals which are obtained on concentrating the solution are purified by recrystallisation from alcohol and afterwards from light petroleum. The acid crystallises in glistening prisms which melt at 92° and become resinous on exposure to air (Barth and Lintner, Ber. 31, 2022). The γ-resin is insoluble in light petroleum. Siller (*l.c.*) finds it to be a mixture of at least two distinct resins differing in carbon content and in solubility in ether.

Mecca or **Opobalsam.** *Balm of Gilead.* This oleo-resin is the balm of the Old Testament and the Greek writers, and is the substance to which the name ‘ balsam ’ was originally applied. The term has, however, with the advance of discovery, come to have another meaning, and is now employed in a generic sense for those resins, oleo-resins, or gum-resins which contain cinnamic or benzoic acids (compare Balsams). Mecca oleo-resin is the product of *Commiphora Opobalsamum* (Engl.), a tree growing in Arabia. Trommsdorff (N. J. T. 16, 62) finds it to consist of *volatile oil*, 30 p.c. ; *soft resin insoluble in alcohol*, 4 p.c. ; *hard resin soluble in alcohol*, 64 p.c. A specimen analysed by Bonastre (J. Pharm. 18, 95) contained only 10 p.c. of volatile oil, and the other constituents were correspondingly higher. In physiological action, the oleo-resin is allied to copaiba and the turpentines.

Hardwickia pinnata oleo-resin. This oleo-resin is an Indian substitute for copaiba. It is derived from a tree nearly related to the *Copaifera*, which inhabits the forests of South Travancore Ghats and South Canara. A specimen examined by Flückiger and Hanbury (Flück. a. Hanb. 233) was a thick, black-looking, viscid fluid, which, when viewed by transmitted light in thin layers, was yellow-green or vinous red, according to the thickness. It had no fluorescence, nor was it gelatinised by heating, as is the case with wood oil. Broughton (Beddows, Flora Sylv. S. India, Madras, 1872, 255) found 25 to 40 p.c. of *volatile oil* $(C_5H_8)_n$, boiling at 225°. From the resins this observer was unable to prepare copaivic acid.

Minjak-lagam. An oleo-resin resembling gurjun was examined by Haussner (Arch. Pharm. 21, 241). It is dingy green by reflected and yellow by transmitted light. It is soluble in alcohol, ether, benzene, chloroform, or carbon disulphide, and yields 33 p.c. of *volatile oil* $C_{20}H_{32}$, boiling at 250°. The *resin* is composed of an acid $C_7H_{14}O_3$ and a neutral constituent.

Sumbul oleo-resin (*Racine de sumbul*, Fr. ; *Sumbulwurzel*, *Moschuswurzel*, Ger.). The root of *Ferula Sumbul* (Hooker), or musk root (Bentl. a. Trim. 131), a perennial plant, inhabiting the mountains of Maghian, in the Khanate of Bokhara. When extracted with ether it yields about 9 p.c. of a *resin*, having a musky odour and ½ p.c. of a bluish *volatile oil.*

Reinsch (Jahrb. pr. Pharm. 6, 300 ; 7, 79 ; 13, 68), by dissolving the resin in alkali and precipitating with water, obtained a salt of *sumbulamic acid*, together with some *angelate*, the two being separated by the easier solubility of the latter in water. Free sumbulamic acid is a turpentine-like mass, which assumes the form of soft yellow needles on standing. Compare also Reinsch and Riecker (Jarhb. pr. Pharm. 16, 12). The existence of an alkaloid *sumbuline* in the resin has not been confirmed (*cf.* Murawieff, Dub. Quart. J. 1852, 255). Sommer (Arch. Pharm. 138, 1) investigated sumbul root. On dry distillation, the oleo-resin gives first a *greenish mobile oil*, smelling like creosote, then a *blue oil*, lighter than water, and with a peculiar, not very agreeable, odour. Together with these, the same observer found crystals of *umbelliferone.*

Turpentine. The oleo-resinous exudates of various species of *Coniferæ.*

Crude or common turpentine. This is derived in Russia and Finland from the *Pinus sylvestris* (Linn.), or Scotch pine ; in Austria and Corsica from *P. Laricio* (Poiret) ; in South-Western France from *P. Pinaster* (Solander) ; and in the United States from *P. palustris* (Mill.), the swamp pine and the Loblolly pine, *P. Tæda* (Linn.) (Flück. a. Hanb. 604 ; Bentl. a. Trim. 256–259). Tschirch and Niederstadt (Arch. Pharm. 239, 167), using the method of examination of resins already described, find the oleo-resin from *Pinus sylvestris* contains : *silveolic acid*, 1·5 ; *silvinolic acids* α and β, 58–60 ; essential oil, 15 ; *silvoresene*, 20–21 ; bitter substance, succinic acid, and impurities, 1–2 p.c. (*cf.* Schkateloff, Chem. Zentr. 1908, i. 2097).

The resin from *Pinus laricio* (Poiret), Austrian turpentine, melts at about 100° and has a yellow colour which on exposure to light becomes red. On boiling with water for a long time and then extracting with ether, caffeic and ferulic acids were obtained and also vanillin (Bamberger, Monatsh. 12, 479). The resin is resolved on digestion with ether into an *α-modification* (80 p.c.), which is soluble in ether, and a *β-modification* (20 p.c.) insoluble in ether. When excess of potash is added to an alcoholic solution of the α-resin or of the crude resin, a colourless crystalline potassium compound is formed which, when treated with hydrochloric acid, gives a powdery precipitate of *pinoresinol.* The caffeic and ferulic acids are in all probability present in an uncombined state (Bamberger, Monatsh. 15, 505). Pinoresinol can be obtained crystalline, m.p. 122°, and has the composition $C_{19}H_{20}O_6$. The β-resin, on purification, forms a chocolate brown powder and appears to have the composition

$$C_{30}H_{30}O_6(OMe)_2.$$

Its properties are those of a tannol whence it is named *pinoresinotannol* (Bamberger and Landsiedl, Monatsh. 18, 481). Tschirch and Schmidt (Arch. Pharm. 241, 570) found 100 parts of the oleo-resin to contain : *laricopinic acid*, 25 ; *laricopinonic acid*, 34 ; essential oil, 35 ; resen, 2 ; water, bitter substance and impurities, 3–4 parts.

Tschirch and Brüning (Arch. Pharm. 238, 630) find in Bordeaux turpentine, the oleo-resin of *P. Pinaster* (Solander), 6–7 p.c. of *pimaric acid* $C_{20}H_{30}O_2$, crystals, m.p. 144–°146° ; 48–50 p.c. of α- and *β-pimarolic acids* ; 28–30 p.c. of essential oil ; 5–6 p.c. of resene ; and 1–2 p.c. of succinic acid, alkaloid, colouring matter, water, and impurities. For concreted French turpentine, common frankincense or galipot, see Resins.

Pinus palustris (Mill.) is the ‘ long leaf pine ’ of the United States and is the chief source of the turpentine and resin prepared there. In 100 parts of the oleo-resin, there are contained *palabienic acid* $C_{18}H_{20}O_2$, m.p. 110°, 5 ; *palabietic acid*, $C_{20}H_{30}O_2$, m.p. 153°–154°, 6–7 ; *palabietinolic acids*, $C_{16}H_{24}O_2$, 53–57 ;

essential oil, 20–22; *paloresene*, 10; bitter substance, impurities, and water, 2–3 parts (Tschirch and Koritschoner, Arch. Pharm. 240, 568).

Canada turpentine, Canada balsam, Balsam of fir. A product of the balsam or balm of Gilead fir, the *Abies balsamea* (Mill.). This is incorrectly called balsam, and it must not be confounded with true balm of Gilead or Mecca balsam (*cf.* Fluck. a. Hanb. 612; Bentl. and Trim. 263). A similar turpentine is obtained from the hemlock spruce, *Tsuga canadensis* (Carr.). This has been investigated by Tschirch and Brüning (Arch. Pharm. 238, 487). 100 parts of the turpentine contain *canadic acid* $C_{19}H_{34}O_2$, m.p. 135°–136°, 13; *canadolic acid* $C_{19}H_{28}O_2$, crystalline, m.p. 143°–145°, 0·3; *α-* and *β-canadinolic acids*, $C_{19}H_{30}O_2$, m.p. 89°–95°, 48–50; essential oil, 23–24; *canadoresene*, 11–12; succinic acid and impurities, 1–2 parts. The oleoresin also contains an alkaloid soluble in water. On dry distillation, formic, acetic, and succinic acids are formed.

Venice turpentine, Larch turpentine. The exudate of the larch *Larix decidua* (Mill.), mostly obtained from the Tyrol. Tschirch and Weigel (Arch. Pharm. 238, 387) have isolated *laricinolic acid*, $C_{20}H_{30}O_2$, m.p. 147°–148° crystals, 4–5 p.c.; *α-* and *β- larinolic acids* $C_{18}H_{26}O_2$, which may be identical, 55–60 p.c.; essential oil, 20–22 p.c.; resene, 14–15 p.c.; alkaloid, colouring matter and impurities 2·4 p.c.; succinic acid, 0·1 p.c. (*cf.* Bamberger, Monatsh, 18, 481; Bamberger and Landsiedl, *ibid.* 20, 755).

Strassburg turpentine is the yield of the Silver fir (*Sapin*, Fr., *Weisstanne* or *Edeltanne*, Ger.), *Abies pectinata* (DC.). The market is supplied chiefly from the Vosges (Flück. a. Hanb. 615; Bentl. a. Trim. 262). In 100 parts the turpentine contains *abienic acid* $C_{13}H_{20}O_2$, m.p. 114°–115°, 8–10; *abietric acid* crystalline, $C_{20}H_{28}O_2$, m.p. 145°–153°, 1·5–2; *α-* and *β- abietinolic acids*, 46–50; essential oil, 28–31; *abietoresene*, 12–16; alkaloid, colouring matter, water, and impurities, 1–2; succinic acid, 0·05–0·08 parts (Tschirch and Weigel, Arch. Pharm. 238, 411).

Hungarian turpentine is obtained from the *Pinus Pumilio* (Haenke).

Chian turpentine is the turpentine of the older writers, and is derived from a small tree, *Pistacia Terebinthus* (Linn.), which inhabits the shores of the Mediterranean and Asia Minor.

Jura turpentine is the product of *Picea excelsa* (Link). The resin melts at about 100° and when boiled with water gives an aqueous extract which contains *p*-coumaric acid and vanillin (Bamberger, Monatsh. 12, 441). Tschirch and Brüning (Arch. Pharm. 238, 616) isolated *piceapimarinic acid* $C_{20}H_{30}O_2$, crystals, m.p. 144°–145°, 2–3 p.c.; *piceapimaric acid* $C_{13}H_{20}O_2$, 1·5–2 p.c.; *α-* and *β- piceapimarolic acids* $C_{25}H_{44}O_2$, 48–50 p.c.; essential oil, 32–33 p.c.; *juroresene*, 10–12 p.c.; succinic acid, alkaloid, colouring matter, water, and impurities, 1–2 p.c. (*cf.* Tschirch and Koch, Arch. Pharm. 240, 272).

The resin from *Pinus halepensis* (Mill.) is used in Greece for preserving and flavouring wine. It has been investigated by Tschirch and Schulz (Arch. Pharm. 245, 156).

The resin oil from *Pinus longifolia* (Roxb.), a tree indigenous to the lower Himalayas, forms a white rather tough opaque mass and has a granular structure which is due to the partial crystallisation of the resin acid. Its odour is extremely pleasant and somewhat resembles that of limonene. Distilled with steam it yields 18·5 p.c. of essential oil (Rabak, Chem. Zentr. 1905, [ii.] 896).

The resins of the Norway pine, *Pinus resinosa* (Solander) and the Douglas fir, *Pseudotsuga Douglasii* (Carr.), have been investigated by Frankforter (J. Amer. Chem. Soc. 28, 1467; 31, 561). Russian 'white pitch,' which is probably the product of *Abies sibirica* (Ledeb.), or of *Picea obovata* (Ledeb.) has been examined by Tschirch and Koritschoner (Arch. Pharm. 240, 584). Brooks (Philippine J. Sci. 1910 [A] 5, 229, has examined the oleo-resin of *Pinus insularis* (Endl.) and the resinous saps from various pines have been investigated by Schkateloff (Chem. Zentr. 1908, i. 2097).

Tar *v.* TURPENTINE. A. S.

OLIBANOL $C_{26}H_{44}O$ is an alcohol contained in frankinscence oil. It forms a yellow oil with an odour of frankinscence, b.p. 217°/20 mm., 333–334°/757 mm.; sp.gr. 0·9596 at 20°; $[\alpha]_D$ −71·50. When warmed with an equal weight of zinc chloride it yields a green oil, b.p. 315°–318°/749 mm.; sp.gr. 0·9400 at 20°.

It is not attacked by alkaline potassium permanganate, but is completely decomposed by chromic acid (Haensel, Chem. Zentr. 1908, i. 1837; *ibid.* ii. 1436).

OLIVE, the fruit of *Olea europœa* (Linn.).

Many varieties are known. The fruit is largely used as a source of olive oil (*v.* OLIVE OIL). It usually consists of about 80 p.c. of flesh and rind, 17·5 p.c. of stone, and 2·5 p.c. of seed. All parts of the fruit contain oil, but the best is obtained from the flesh. According to König, the following gives the average composition of the various parts of the fruit:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Flesh	30·1	5·2	51·9	10·5	2·3
Stone	9·2	3·5	2·8	83·3	1·1
Seed	10·6	18·6	31·9	36·7	2·2

whilst the ash has the following percentage composition:—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Flesh	80·9	7·5	7·5	0·2	0·7	1·3	1·1	0·7	0·2
Stone	58·8	6·6	7·5	0·4	0·8	16·7	3·3	1·3	4·7
Seeds	30·3	2·0	30·4	1·2	0·1	28·2	2·4	5·4	0·1

The fruit has an insipid, bitter taste, and is usually pickled before being eaten, salt and spices being used for the purpose. The following are American analyses of the edible portions of pickled olives:—

	Water	Protein	Fat	Carbohydrates and fibre	Ash
Green olives	58·0	1·1	27·6	11·6	1·7
Ripe olives	64·7	1·7	25·9	4·3	3·4

Ground olive stones or 'poivrette' have been used to adulterate pepper (*v.* Wynter Blyth, Foods; also Martelli, Staz. Sper. Agrar. 1895, 28, 53). For results of the examination of olive leaves and bark *v.* Canzoneri (Gazz. chim. ital. 1906, 36, [ii.] 372) and Power and Tutin (Chem. Soc. Trans. 1908, 93, 891, 904). According to Bourquelot and Vintilesco (Compt. rend. 1908, 147, 533), olives contain a glucoside—

oleoeuropein—a yellow powder with bitter taste, hydrolysable by emulsin, which is present in the fruit, leaves, and bark, yielding dextrose (*v.* also Power and Tutin, Pharm. J. 1908, [iv.] 27, 714; and Vanzetti, Atti. R. Accad. Lincei, 1909, 18, ii. 188). H. I.

OLIVE OIL. Olive oil is obtained from the fruits of the olive tree, *Olea europœa* (*sativa*), L. The olive tree is probably indigenous to Western Asia, but was at an early date introduced into all the countries bordering on the Mediterranean. Recently the cultivation of the olive tree has been introduced into California, South Africa, and Australia. The olive tree thrives best in a sub-tropical climate, and its successful cultivation extends in Europe as far north as latitude 44½°. In America, it scarcely extends to latitude 34°. Attempts have also been made in several parts of India to cultivate the olive tree, but although it grows well and flowers, the fruit seldom matures.

The olives intended for oil production are gathered just before the period of maturity, as the oil obtained from the barely ripe fruit is much superior in quality to that obtained from fully ripe or over-ripe fruits.

The proportion of oil in the fruit goes on increasing to the maximum found in fruit which has reached complete maturity; it then decreases slowly. The ripe olives contain up to 70 p.c. of oil. This figure is, however, an exceptional one, the fleshy part of the best cultivated olives containing only from 40 to 60 p.c. of oil. The Algerian olives vary in their proportion of oil within wide limits, from 10·03 p.c. to 32·98 p.c. (in the Jemmap olives). The Californian olives also yield much smaller quantities of oil than the best cultivated European varieties.

The technical processes employed for the production of olive oil are still represented by both the oldest and crudest processes (see preparation of Oils, Fixed, and Fats) and by the most modern methods adapted to large-scale working.

The very finest oils are obtained from hand-picked fruits by first crushing them in a mill without breaking the kernels. Exceptionally fine qualities are prepared by peeling hand-picked fruits and pressing lightly, after carefully removing the kernels. The crushed marc is then expressed in a hydraulic press; the oil so obtained ranks as the best edible oil—'*huile vierge*,' '*huile surfine*.' Commercial brands of this quality are 'Provence Oil,' 'Aix Oil,' 'Nice Oil,' 'Var Oil.' The oils sold as 'Finest Tuscan Cream,' 'Riviera Oils' (Genoa), 'Bari Oils' may also be ranked amongst the best edible oils, although they are distinctly lower in value than the oils of the South of France, and come nearer the following somewhat inferior quality. This is obtained by pouring some cold water on the marc, after the pressure in the hydraulic press has been released, and pressing again. Such inferior oil is also sold as an edible oil, either alone or mixed with the oil of the first expression as '*Salad Oil*,' '*huile fine*,' '*huile de table ordinaire*.'

The pulp left in the press yields, after mixing with hot water and pressing once or twice, a bright oil used for lubricating purposes, as burning oil, and for soapmaking.

In most of the smaller works, the kernels are not removed and are crushed together with the fruit. In large establishments, however, the kernels are removed and crushed separately, yielding olive kernel oil. (See tables Oils, Fixed, and Fats). The repeatedly pressed pulp ('grignons') still contains a considerable amount of oil, varying from 10 to 22 p.c. This pulp is beaten with hot water in special mills—*moulins de ressence*—resembling edge-runners. The oil cells are thereby further broken up; the ground mass, together with the water, is then allowed to run into a series of vessels, arranged in tiers, where the water separates from the oil and broken cellular tissues. The oil and the tissue rise to the surface, to be skimmed off, whilst the heavier crushed kernels fall to the bottom. The latter are known as '*grignon marc blanc*.' The emulsion of oil and cellular tissue, which has been skimmed off, known as '*grignon marc noir*,' is heated and subjected to a fresh expression in a hydraulic press. The oil so obtained is termed 'huile de ressence,' and the pressed residue is known as 'tourteau de ressence.' The *huile de ressence* is allowed to rest in large tanks at a somewhat elevated temperature, when a clear oil separates on the top—'*huile claire de ressence*'—and a lower layer of thicker oil 'Olive Oil Grease' (*pâte de ressence*) settles out.

In some establishments the marc, instead of being boiled with water, is thrown into pits where the pulp undergoes a kind of fermentation, whereby the oil is set free and gradually rises to the top. Oil of this kind is known as '*huile d'enfer*.' The name 'huile d'enfer' is applied also to oil which has settled out from the waters obtained from the press after moistening and boiling the pulp, which has been stored in underground cisterns ('enfers'). To this class of oil belong the bagassa (bagasse) oils, which are obtained principally in Portugal from fermented marc. These oils contain as much as 60–70 p.c. of free fatty acids.

'Tournant oil' is a commercial product of the quality of the 'huiles d'enfer,' obtained from the fermented marc of expressed olives; it contains a considerable quantity (up to 26 p.c.) of free fatty acids, and therefore forms a very complete emulsion (which constitutes its value) with a solution of sodium carbonate. Such Turkey-red oil was first employed for this purpose by Haussmann, 1792, and then recommended by Koechlin Frères.

The cake remaining after the removal of the *huile de ressence*, termed 'tourteau de ressence,' or "sanza," is finally deprived of its last content of oil by extracting with solvents, sometimes after a preliminary drying. The solvent usually employed in France and Italy is carbon disulphide. Hence, these oils are termed 'sulphocarbon oils,' 'sulphur olive oils.' They have a deep green colour, due to the chlorophyll which has been extracted by the solvent, and contain the more solid portion of olive oil which has remained behind in the pulp. These oils contain large proportions of free fatty acids as also notable amounts of lactones.

For the physical and chemical characteristics see tables Oils, Fixed and Fats.

Some Tunisian olive oils are so rich in glycerides of solid fatty acids that they deposit 'stearine' on standing. [Hence they are unsuitable for table oils. Therefore, such Tunisian oils must be 'demargarinated' (see Oils, Fixed, and Fats).

The extracted cake is sold as manure. The press residues which have yielded superior kinds of olive oil, would be suitable for feeding cattle; but as the oil, which can be easily recovered by extraction—about 10 p.c. of the residues—is too valuable, olive cakes are only used locally and to an inconsiderable extent as cattle food.

Olive oil typifies eminently a non-drying oil. On account of its comparatively high price, it is adulterated to an enormous extent. How far the blending of various olive oils of different qualities should be considered as an adulteration must be decided in each given case. Undoubtedly the 'finest Nice oil,' which has been prepared by blending a genuine Nice oil with Tunisian oils or other olive oils, must be considered as of inferior quality. At present, olive oil is most frequently adulterated with arachis oil, as the detection of this oil offers greater difficulties to the analyst than those oils which were previously used to a much greater extent, viz. cotton seed oil, sesamé oil (rape oil). The adulteration with hydrocarbons has practically ceased for the simple reason that they are too easily detected. J. L.

OLIVINE. An abundant rock-forming mineral consisting of magnesium orthosilicate with variable amounts of ferrous orthosilicate, $(Mg,Fe)_2SiO_4$. Crystals are orthorhombic, but of rare occurrence; granular masses are more common. The colour ranges from pale yellowish-green to brown, depending on the amount of iron present. The mineral is decomposed by hot hydrochloric acid with separation of gelatinous silica. It occurs in many basic and ultra-basic rocks of igneous origin (basalt, gabbro, peridotite, &c.), and it is an important constituent of stony meteorites. Deposits of diamond, platinum, chromite, and nickel-ores are usually associated with olivine-rocks; and by the weathering of these rocks, serpentine and associated deposits of steatite, magnesite, and meerschaum are formed. The only direct practical application of olivine is as a gemstone; the clear, transparent stones are yellowish-green (chrysolite) or rich olive-green (peridot) in colour. Such material comes mainly from the island of St. John in the Red Sea, and it is also collected from ant-hills in Arizona and New Mexico. L. J. S.

OMEIRE. A drink resembling koumiss, prepared by the natives in South-West Africa by filling gourd bottles, which contain some fermented milk, with milk, shaking well and allowing to stand. It is a thick, semi-coagulated liquid, possessing a pleasant, wine-like smell, and a slightly sour taste; it contains a little alcohol (Arch. Pharm. 1887, 744).

OMEROL *v.* Synthetic Drugs.

ONION SKINS. The outer dry skins of the bulb of the onion, *Allium Cepa* (Linn.), were formerly employed for dyeing purposes. According to Leuchs (Farben und Färbekunde, 1825, i. 434), the outer skins of onion bulbs, which are of a brownish-orange colour, have long been used in Germany for dyeing Easter eggs yellow and in conjunction with alum for dyeing woollen, linen and cotton materials. The colour is fast and particularly brilliant.

The dyestuff present is in reality *quercetin*, and this can be isolated from the skins to the extent of 1·3 p.c. by mere extraction with boiling water (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1295). A. G. P.

ONOFRITE *v.* Mercury; also Selenium.

ONONIS ROOT. Contains a glucoside *ononin* $C_{25}H_{26}O_{11}$, forming colourless needles, m.p. 210°, decomposed by dilute acids into dextrose and *ononetin* (*v.* Hemmelmayr, Monatsh. 1902, 133; 1903, 132).

ONYX. A variety of chalcedonic silica differing from agate only in the straightness and parallelism of its differently-coloured layers, and so suitable for engraving as cameos. The alternate bands of colour are usually white and black, or white and red; in sardonyx they are white and brown. Most of the onyx with intense differences in colour, as now placed on the market, has been coloured artificially by chemical means (*v.* Agate). L. J. S.

ONYX-MARBLE, Algerian onyx, Mexican onyx, or 'Oriental alabaster' (also called 'onyx' in ancient times and in the marble trade of the present day). A banded, translucent variety of fibrous or granular calcite, or marble, susceptible of a fine polish, and much used, both in ancient and modern times, as an ornamental stone. The colouration, which is distributed in bands or cloudy patches, is due to the presence of ferrous carbonate and ferric hydroxides, and to a less degree of manganese oxides and organic matter. For example, a green marble from Arizona contained 4·27 p.c. $FeCO_3$, and in its brownish-red (oxidised) portions 1·22 p.c. $FeCO_3$ with 3·53 p.c. Fe_2O_3. The percentage of calcium carbonate rarely falls below 90. Onyx-marble is quarried in Algeria, Mexico, and Arizona. (*See* G. P. Merrill, The Onyx Marbles: their Origin, Composition, and Uses, both Ancient and Modern, Rep. U.S. Nat. Mus. for 1893, 1895, 539; G. P. Merrill, Stones for Building and Decoration, 3rd edit., New York, 1903. L. J. S.

OOPHORIN *v.* Synthetic Drugs.

OPAL. Colloidal silica, occurring native in botryoidal and stalactitic forms, or as irregular masses occupying cracks and cavities in certain rocks. It is softer and less dense than quartz; its hardness being only 5½ to 6½, while its sp.gr. varies with the impurities present from 1·9 to 2·3. Being non-crystalline it should exhibit single refraction, but many varieties, especially of noble opal, are strongly birefringent; the anomaly being probably due to the strain set up by unequal contraction in different directions during the solidification of the gelatinous mass. Opaline silica is nearly always hydrated, but the proportion of water varies from about 2·5 to upwards of 10 p.c. Von Kobell found that the noble opal of Hungary lost 10·94 p.c. when strongly heated. The substance is almost wholly soluble in a hot solution of potassium hydroxide.

The purest opal, known as *hyalite* or *water-opal*, occurs as colourless, transparent masses, resembling glass. *Semi-opal* is a name applied to the dull, opaque varieties, generally more or less impure. *Menilite* or *liver-opal* is a brown opaque mineral, occurring as nodules in the Tertiary strata of the Paris basin, especially at Menilmontant. *Wood-opal* is simply wood fossilised with opaline silica, and retaining the ligneous structure, which produces a pleasing effect when the substance is cut and polished; hence it is used in slabs as an ornamental stone. *Hydrophane* is an opal which, when dry, is opaque and dead white, but absorbs water rapidly when moistened, becoming transparent and sometimes exhibiting a play of colours. A fine variety found in Colorado has been brought into use under the name of 'magic stone.' *Common opal* is a general term for any opal which does not display sufficient colour to recommend its employment for decorative purposes. According to its appearance it often receives trivial names, such as milk-opal, wax-opal, &c. *Fire-opal*, found chiefly in Mexico, exhibits a brilliant hyacinthine or orange colour, which renders it of some value in jewellery. But the finest variety of the opaline group of minerals is the *precious* or *noble opal*, a substance which is unique in exhibiting by reflected light a vivid play of iridescent colours. The cause of this phenomenon has been studied by Brewster, Crookes, Behrens, Lord Rayleigh, and others. By most authorities it has been referred to the presence of numerous microscopic pores, fissures, or striæ in the interior of the stone; but Behrens considers it due to the interposition of thin lamellæ of opaline matter having a different index of refraction from that of the matrix (Sitz.-Ber. Akad. Wiss. Wien. Math.-naturw. Cl. 1871, 61, 519). If the colours proceed from distinct patches, like a brilliant mosaic, the stone is termed in trade *harlequin opal*. Precious opal is a mineral of very limited distribution. The oldest mines are those on the Dubnik Hill, near the village of Czerwenitza (Hungarian, Vörösvágás), near Eperjes in northern Hungary, where the opal occurs in a matrix of andesite. Slabs of matrix, or 'mother-of-opal,' enclosing brilliant particles of the gem, are polished as ornamental stones. Opal is also found at Gracias-á-Dios, in Honduras; at Queretaro, in Mexico; near the Barcoo river, and several other spots in southern and central Queensland; and at White Cliffs and other districts in northern New South Wales. The Queensland opal occurs in cracks in nodules of jaspery brown iron-ore, and is remarkable for its brilliant blue and green colours; that of White Cliffs, discovered in 1889, occurs in a white sandstone of Cretaceous age. Opals are usually cut *en cabochon*, *i.e.* with a convex surface, but the Queensland stone, occurring in thin layers, lends itself to cameo-work, the brown ferruginous matrix forming an effective background. 'Black opal,' enclosing patches of manganese oxide and exhibiting a brilliant play of colours, has recently been found at Lightning Ridge in northern New South Wales.

In addition to the compact forms of opal mentioned above, there are also loose and friable forms of opaline silica represented by silicious sinter or geyserite (deposited by the hot springs of Iceland, New Zealand, and the Yellowstone Park in Wyoming) and by diatomaceous earth or kieselguhr (*q.v.*) (consisting of the silicious skeletons of diatoms and radiolaria).

L. J. S.

OPHICALCITE *v.* MARBLE.

OPIAURIN. Opianic acid and phenol, when heated together with strong sulphuric acid, give rise to an intense yellow-red dye. The reaction takes place between the aldehyde group of the acid and the phenol

$$C_6H_2(OCH_3)(CO_2H)(CHO)+2C_6H_5{\cdot}OH$$
$$=H_2O+C_6H_2(OCH_3)_2{\cdot}(CO_2H){\cdot}CH(C_6H_4OH)_2$$

This compound *leucopiaurin* is oxidised during the process to opiaurin $C_{22}H_{18}O_6$. The best results are obtained by stirring an intimate mixture of opianic acid and phenol into sulphuric acid (60°B.), and keeping the mixture well cooled. After 24 hours it is thrown into a large quantity of cold water, and the precipitate, when washed and dried, freed from tarry matters by extraction with hot benzene. Opiaurin is soluble in alcohol, ether, and glacial acetic acid, insoluble in benzene and light petroleum. It can only be obtained in the amorphous condition. It dissolves in alkalis with a purple colour; the solution in alcoholic ammonia becomes brownish-yellow on heating, but the purple colour returns on cooling.

Sulphurous acid does not reduce it. Opianic acid reacts in a similar way with other phenols, and the reaction can be used to detect the presence of opianic acid, as also of an aldehyde group in aromatic compounds; the reagents are separately dissolved in an excess of cold sulphuric acid; on mixing the solutions the colouration takes place at once (C. Liebermann and P. Seidler, Ber. 20, 873; J. Soc. Chem. Ind. 6, 541).

OPIUM.

Origin.—Opium is the milky juice of the unripe capsules of *Papaver somniferum* (Linn.) or opium poppy, obtained by incision and inspissated by spontaneous evaporation. The plant (*v.* Bentl. a. Trim. 18) is perhaps indigenous to Asia Minor and neighbouring districts of South-Eastern Europe and Western Asia; but it is now cultivated more or less throughout all temperate and sub-tropical countries. It exhibits, however, morphological differences. The two most important varieties which, according to Boissier, are cultivated for the production of opium, are *glabrum*, with subglobular capsules and ten to twelve stigmata, and *album*, with egg-shaped capsules and without apertures (Flora Orientalis, 1867, 1, 116). The former is grown in Asia Minor and Egypt, and the latter in Persia and India. But besides these varieties there are minor distinctions, the petals in the same variety differ in colour, and may be white, red, or violet, with a dark-purplish spot at the base in most cases. The seeds are white or dark-coloured, and contain from a third to half of their weight of fixed oil. The capsules are provided with a lacticiferous system from which the juice exudes when they are incised. This milky juice is present in the plant in all countries where it has been grown, and opium may be collected provided that the rainfall is not too great and the temperature neither arctic nor entirely tropical. That its production is confined for the most part to Asia Minor, Persia, India, and China, is determined by other considerations such as the value of land and the cost of labour.

History.—The drug was known early in the third century B.C. to Theophrastus. Scribonius

Largus, in the first century A.D., describes the method of preparing it and remarks that it should only be made from the capsules; for, as Dioscorides, writing a little later, points out, two sorts of opium were in use at that period. One of these, the opium proper, was prepared from the capsules, and the other, 'meconium,' was extracted from the entire plant by means of a solvent. Similar accounts may be found in the works of Pliny and other Latin writers. The opium of the classical period, and indeed the only variety known till the twelfth century, was exclusively that of Asia Minor. The nations of the East appear to have learned of opium from the Arabians, and it seems probable that the use of the drug was favoured by the Mahomedan prohibition of alcohol. They are supposed to have introduced the drug into China in the ninth century. Egyptian opium, 'Opium Thebaiacum,' is mentioned by Simon Januensis about the end of the thirteenth century. At this time, and three centuries later, according to Prosper Alpinus, meconium was still prepared in the Thebaïd in Upper Egypt.

In India opium was collected early in the sixteenth century. Barbosa describes a variety produced in Cambay. Pyres, the first European ambassador to China, writing in 1516, mentions three varieties of opium, obtained respectively from Egypt, Cambay, and from the kingdom of Coûs. The last-mentioned district is Kus Behár, south-west of Bhotan in Bengal. Garcia d'Orta, a little later, remarks that Cambay opium is chiefly derived from Malwa. The opium production was a State monopoly in India under the Moguls, and after the victory of Clive at Plassy in 1757 the monopoly passed into the hands of the East India Company. The manufacture then greatly increased, and it has gone on increasing until within the last few years. It was during the seventeenth century that the first accounts reached us of the production of opium in Persia. Kämpfer found that the 'theriaka,' which had long been held in high esteem by neighbouring nations, was made by mixing the finer sorts of opium with spices.

The Chinese obtained their opium from India. Until the beginning of the eighteenth century it formed part of the return cargo of their junks. The importation was then small, and it was used almost exclusively in medicine as a remedy for dysentery. The imports did not reach 1,000 chests (Malwa chests contain one pecul, or 133⅓ lbs., Patna chests 160 lbs.) until 1767, when the trade was mostly in the hands of the Portuguese. In 1790, under the East India Company, it had become 4,054 chests. It was at this time that the habit of smoking began to spread in China. To promote the trade the East India Company established an opium depôt of two ships, which lay off the island of Macao, at the entrance to the Canton river. The importation went on increasing, notwithstanding that it was forbidden by the Chinese Government in 1796, and that an edict was issued in 1820 prohibiting opium-laden ships from entering the river. The trade, which between 1820 and 1830 had risen to 17,000 chests annually, then assumed a contraband character. Complaints, however, continued, and when in 1839 it was decided to enforce the law, this, together with other difficulties, led to a war with England which terminated in the treaty of Nanking in 1842. By this treaty five ports were opened to foreign trade, and the island of Hong Kong was ceded to the British Government. The export of opium from India into China, which in 1870 amounted to 55,000 chests, increased to 95,000 chests in 1880. Owing to Chinese home production, however, the importation of Indian opium then began to decrease until in 1890 it fell to 70,000 chests and in 1907 to 50,000. Recently, an important movement has arisen in China to put a stop to opium smoking throughout the Empire, and to this end to gradually terminate both the home production of the drug and its importation from India. With regard to the Indian importation, the wish of China has been met by the Government of this country, and notwithstanding the serious loss which it entails to the revenue of India, which in 1880 amounted to Rs.8,500,000, and to the Indian poppy cultivators, the British Government, reciprocating the views expressed by the Chinese, entered into an agreement, the effect of which, it is hoped, will be that both the Chinese production and the Indian exportation to China will be made to decrease together, and this so rapidly that, according to well-informed authorities, both will come to an end in a few years' time.

Numerous attempts had been made during the seventeenth and eighteenth centuries to prepare active condensed extractives from opium, but no constituent of a definite nature was discovered until the beginning of the present century. Derosne in 1803 noticed a separation of crystals on diluting an aqueous extract of opium (Ann. Chim. Phys. [i.] 45, 257). Their basic character was demonstrated by Robiquet in 1817 (*ibid.* [ii.] 5, 275), and the compound is now called *narcotine*. Derosne noticed that opium solutions are precipitated by alkalis, but thought that the precipitate was the same compound which he had previously isolated. Seguin in 1814 described what was probably the chief active constituent of opium (*ibid.* [i.] 92, 225), but to isolate in a definite form and make known the basic properties of *morphine* was reserved for Setürner, an apothecary of Eimbeck in Hanover, whose work extended from 1805 to 1816. During the same inquiry, in 1806, Setürner also brought to light *meconic acid* with which the morphine is combined. Morphine was the first compound known belonging to the class of vegetable bases, which has since become so important; for although narcotine was isolated just before, its properties as an alkaloid were not ascertained until afterwards. Further historical and other details will be found in the article on opium in 'Pharmacographia' (Flück. a. Hanb. 272), from which many of the facts given have been obtained.

Production.—Asia Minor. Opium is collected in Asia Minor for the most part by small peasant proprietors, the largest quantity being obtained in those countries lying to the west, and having Smyrna and Constantinople for their ports of shipment. The product of these countries is the *Turkey* opium of English commerce, and of all available varieties it is the richest in morphine. The poppy grown is the variety *glabrum* of Boissier. The flowers are purplish or sometimes white, and the seeds white to deep violet. The plant grows in elevated as well as lower situations, and requires a moist soil and much attention and skill on the part of the cultivator. Details of the mode of preparing the soil and management of the crop are given by Maltass (Pharm. J. [i.] 14, 395) and Heffler (*ibid.* [ii.] 10, 434), and in the official directions drawn up by the Turkish Government for the promotion of the opium culture in Macedonia (*ibid.* [iii.] 13, 918). The crop is sometimes destroyed by early frosts, drought, or the attack of locusts. The seed is sown from November to March, and the flowering takes place from May to July. In this way successive crops of capsules become ready for incision during a period of about three months, and a saving in the cost of labour is effected.

In the course of a few days, after the petals have fallen, when the capsules are some 1½ inches in diameter, they are ready for incision. This is done transversely around the middle by means of a knife. The operation is one requiring skill, for if the incision be not deep enough an incomplete flow of juice results, and if it be too deep some of the juice is lost inside the capsule. The incisions are made in the afternoon, and the exuded and partly hardened juice is collected the following morning. It is scraped off and placed on a poppy leaf. Masses of hardened juice thus obtained are allowed to stand in the shade to dry still further, and are then made into lumps of varying size and sold to dealers in the towns. By these the opium is manipulated into cakes suitable for the market, enveloped in poppy leaves and packed in bags, into which Rumex fruits are thrown to prevent the cake adhering together. The bags are then sealed and transmitted to Smyrna and Constantinople, where they are opened in presence of the seller, the buyer, and a public examiner. The examiner scrutinises the drug piece by piece, and by its physical characters classifies it as (1) *prime*, (2) *current*, and (3) *chiqinti*. The 'current' constitutes the great bulk of mercantile opium. An important addition to the profits of the opium culture is the sale of poppy seed, from which the oil is expressed and used for a variety of purposes. It is a bland, limpid, drying oil, of a pale colour (Maltass; Heffler; Scherzer, Pharm. J. [iii.] 11, 835).

Good Smyrna opium when dry contains 12 to 15 p.c. of morphine. If less than 10 p.c. is found in a specimen adulteration may be suspected. The opium used in medicine in this country when dried is required to contain not less than 9·5 and not more than 10·5 p.c. of morphine (Brit. Pharm. 1898). The dried Turkey opiums examined by Guibourt contained from 11·7 to 21·5 p.c. or a mean of 14·7 p.c. of morphine (J. 1862, 374). Of ninety-two specimens examined by Fayk Bey, the highest was 17·2 p.c., and half of them contained more than 10 p.c. (Flück. a. Hanb.). Bulgarian opium, analysed by Theegarten, gave:—Küstendil, in large lumps, 4 to 10 oz., 17·69 p.c.; Lowtscha, 11·90 p.c.; Halitz, 7·25 p.c. (Pharm. J. [iii.] 11, 896; 13, 342).

Turkey opium, as it appears in English commerce, consists of rounded masses, generally from ½ to 2 lbs. in weight but sometimes larger or smaller. Externally it is covered with poppy leaves and Rumex 'chaff.' It has a bitter taste, and peculiar, though not altogether disagreeable, odour. The following are among the more important districts, the products of which come to Constantinople:—Bogaditz; Karahissar-Sahib; Kutchaya; Balukhissar; Kurkagatsch; Ismid or Ghéve, the product of Geiveh; Beybazar; Angora; Malatia; and Tokat. In addition to these the Constantinople market receives the opium of Macedonia and, until recently at least, small supplies from Bulgaria. The cultivation of opium in Macedonia commenced in 1865 from seeds brought from Karahissar. In 1882 the districts of Kotchava, Straumnitza, and Tikvish exported 135,000 lbs. by way of Salonica, whence it is termed collectively Salonica opium. The opium districts in Bulgaria are Küstendil, Lowtscha, and Halitz. The produce is mostly consumed by local pharmacy; but, while the country remained under Turkish dominion, any surplus found its way to Constantinople.

The market at Smyrna receives the products of Afium Karahissar, Ushak, Akhissar, Tanshauli, Isbarta, Koniyeh, Bulladan, Hamid, Magnesia, and that collected in the neighbourhood which is known as Yerli.

In the English market, Turkey opium is divided into three classes, known as 'shipping,' 'druggists',' and 'manufacturing' opium. As *shipping* opium are classed those varieties which contain the least proportion insoluble in water, and which yield the greatest quantity of extract adapted for smoking. These are the opiums of Malatia, Tokat, Salonica, Balukhissar, Kurkagatsch, Bokaditz, and 'prime' Angora and Yerli. This opium is exported to China, Peru, the West Indies, British Guiana, Brazil, and for reshipment, to the United States. *Druggists'* opium is selected for a high percentage of morphine and includes the varieties which are used in medicine. It has a firmer consistence and a darker colour than the others. In England the products generally chosen are: Beybazar, Yerli, Karahissar, including Adet, Amasia, Akhissar, and 'current' Smyrna and Angora; for America, Ushak, Yerli, and Karahissar; and for the Continent, Ghéve. *Manufacturers'* opium is used for the preparation of alkaloids and includes 'chiqinti,' Persian, and other low-priced opiums (Holmes).

Among the various adulterants which have been detected, from time to time, in Turkey opium are: sand, clay, grape-juice thickened with flour, fig-paste, liquorice, half-dried apricots, tragacanth, pounded poppy capsules, and even turpentine, stones, and bits of lead.

Of late years there has been a great decrease in the production of opium in Asiatic Turkey attributed entirely to the low prices.

Egypt. Only a small quantity of opium is now exported from Egypt. Owing to its inferior quality it is not regularly imported into England. Small consignments are, however, sent to Turkey and other countries on the Mediterranean sea-board. It is cultivated in Upper Egypt near Esneh, Kenneh, and Assiout, the ancient Thebaïd. Allen, in 1861, describes the collection of opium from a white poppy. The capsules are slit twice transversely, and the juice collected the following day with a sort of scoop-knife, and placed on a leaf, in the sun, to harden (Pharm. J. [ii.] 4, 199). The product is sent out in cakes, enveloped in poppy leaves, but without Rumex fruits. According to information supplied to Martindale, the best opium is collected at Akmim, on the right bank of the Nile, 320 miles above Cairo; while at Assiout, 250 miles above, an inferior quality is produced. A piece of Akmim opium, in the form of a hard flat cake, four inches in diameter, and one inch in thickness, contained 7·24 p.c. of morphine. There was the mark of a leaf adhering to it, and it had a rough and irregular appearance. A specimen from Assiout, consisting of segments of a cake, much softer and evidently adulterated, yielded only 0·6 p.c. of morphine (Pharm. J. [iii.] 19, 743). Other specimens have given 5·8 to 12·2 p.c. (Guibourt, J. 1862, 374), 3·4 to 3·9 p.c. (Petermann, J. 1866, 704), and 5·8 p.c., together with 8·7 p.c. of narcotine (Flück. a. Hanb.). It has also been shown by Gastinel that opium can be made in Egypt containing 11 to 12 p.c. of morphine. The fact that it generally contains only half that proportion is due partly to an over-moist soil and unskilful collection, but also doubtless to adulteration (Flück. a. Hanb.).

Persia. The quantity of opium produced in Persia has until recent years been small and inferior in quality. The strongest, the *Teriak-e-Arabistani*, was obtained from Dizful and Shuster, in Khuzistan. A good quality was produced near Sari and Balfarush, in Mazandaran, near the Caspian, and in the southern province of Kerman. Inferior sorts came from Shahabdulazim, Kashan, and Kum. The cultivation extends into Turkestan, where a sort of meconium is also manufactured. Part of these products went overland to China, by way of Bokhara, Khokan, and Kashgar, and another part found its way to Constantinople, by way of Trebizond, to be sold as Turkey opium (Flück. a. Hanb.). More attention is, however, now given to the cultivation of the plant and the collection of the juice, and there is less adulteration, the result being a great increase in the trade. The poppy cultivated is the variety *album* (Boissier), having roundish ovate capsules. Shiraz and Behbahan, the latter in the neighbourhood of Bushire, and other new districts, furnish supplies (Pharm. J. [iii.] 11, 804), and old centres like Kum, Teheran, and Yezd, have improved the quality of their product (*ibid.* [iii.] 15, 113, 430). Ispahan has now become the chief centre of the opium cultivation, the other important districts being Shiraz, Yezd, Khonsar, and also Khorasan, Kermanshah, and Fars.

About the year 1870 a regular export trade of Persian opium was established by water from the ports of Bushire and Bunder Abbas, in the Persian Gulf, and the quantity exported increased rapidly. By far the greater part is now shipped from these ports direct to Hong Kong, where it competes in the market with the product of Patna, Benares, and Malwa. A smaller part is shipped to the Straits Settlements, and the rest to England. A less important trade continues with Constantinople, by way of Trebizond and Samsun, and part of the opium made in Teheran, Tabriz, and Kermanshah, also finds its way to Smyrna.

In China, Persian opium has, to a certain extent, replaced Indian opium owing to its being manufactured to suit the Chinese taste. After it has been once smoked the residue in the pipes, if the opium is of good quality, can b used mixed with fresh opium some six or seve times, whereas Benares opium cannot be use thus more than once. The smoke of the Persia opium is milder and in consequence mor suitable to a tropical climate (J. Soc. Chem. In 1892, 646). It is impossible to determine th opium production of Persia as no statistics ar kept, but in the season 1905–1906, the value o the opium exported to different parts of th world was over £173,000.

The greatly increased consumption of opiu in Persia has led to the extension of the cultivation of the poppy over the whole country.

The capsules are ready for cutting at th beginning of June. Since the lightest colour opium commands the best price in the market the incisions in the poppy heads are made a sunset and the exuded sap is collected befor sunrise, as sunlight discolours the product Vertical incisions are made, and the juice i collected and conveyed to the market in coppe vessels. There it is manipulated to suit th tastes of buyers in Hong Kong and London whither it is exported between September an January. One of the most celebrated product is that of the village of Kupa, a short distanc east of Ispahan.

The opium for home consumption in Persi is prepared by adding 20 p.c. of foreign matter t the crude opium after its volume has been reduced one-sixth by evaporation. The adde material is usually ‘sarcocolla,’ the resin o *Penœa mucronata* (Linn.), but sometimes boiled extract of dried poppy heads, the seed o wild rue, and an extract obtained by steepin fresh poppy leaves in water, are added. Th mixture is then boiled slowly for 3 hours wit constant stirring, and the paste thus obtained i kneaded and rolled into small sticks for th market. The opium left in the pipes afte smoking is prepared for further consumptio by being mixed with about 10 p.c. of raw opiu and is then smoked as *Teriak-suchte* (burn opium) or is eaten in the form of pills. Th opium for export which is sold in lumps is prepared from the raw opium by drying until it bulk is reduced by about a quarter, an then adding from 50–70 p.c. of grape juice o other unknown ingredients. This opium i homogeneous and it does not present a granula appearance like the Turkish opium. Morphine estimations show that good samples contai about 15 p.c. and the dry extracts contain about 18·5 p.c. of morphine (Siedler, Chem. Zeit 26, 920; Stahl, *ibid.* 32, 804).

India. Opium is one of the most important products of India. It is a State monopoly of the Bengal Government in Behar and Benares, and is cultivated free in the Malwa and other districts of the native States, whence on arrival in British territory it pays duty.

The area devoted to poppy cultivation in Bengal comprises the large central tract of the Ganges, about six hundred miles in length and two hundred in breadth. It extends east and west, from Dinajpur to Agra, and north and south, from Gorakhpur to Hazaribagh. According to Watt, the average annual area actually occupied by the poppy in Bengal for the last thirty years has been 490,000 acres. The State does not restrict the cultivation of opium; but it is a monopoly in the sense that what is cultivated must be sold to the Government at a price agreed upon beforehand. One object of these regulations is to prevent the neglect of cereals, for the poppy culture is very much more profitable; in Malwa it is said to realise from three to seven times as much as the ordinary crops. The opium of Behar and Benares is sold at auction in Calcutta, part is retained for consumption in India, but the greater portion is shipped to China.

The remainder of the opium raised in India is produced by the native States. The most important centre is the broad tableland of the Malwa and the adjoining slopes of the Vindhya Hills. The opening of the railway has given a great impetus to the cultivation in Rajputana and Malwa. Smaller quantities are produced in the Punjab, not only in the plains, but to the eastward of Lahore, in the valley of Bias, as high as 7500 feet above the sea. Kulu also produces excellent opium. It is raised in Nepal, Basahir, and Rampur, and at Doda Kashtwar, at the base of the Himalayas, in the Jammu territory, from which districts it is sent to China overland (Flück. a. Hanb.). Nearly all the opium produced in the native States, however, enters British territory, and pays a duty according as it comes from the districts of Ahmedabad, Ajmere, or Malwa. It is then sent to Bombay, whence, under the general name of Malwa opium, it is shipped to China.

The poppy grown in India is the same variety as that of Persia. The same requirements of soil and climate have to be met. In addition to the dangers to which the crop is exposed in Asia Minor the plant in India is liable to the attack of a parasitical species of broom rape, *Orobanche indica*, which attaches itself to the roots and causes the plant to wither. The factory for the Behar district is at Patna, and for the Benares district at Ghazipur, where the Government agents are stationed. In Benares and Behar the seed is sown in November, and the capsules are ready in February or March. They are then incised or scarified vertically, by means of an instrument called a 'nushtur,' constructed of several blades bound together (*cf.* plate, Pharm. J. [i.] 11, 207). This operation is repeated, in the course of a few days, on different sides, each capsule being scarified from two to six times. The next morning the juice, which has exuded, is scraped off by the use of a sort of concave trowel made of sheet iron, called a 'seetoah,' and collected in earthen pots. The poppy capsules are afterwards utilised in a variety of ways and the oil expressed from the seeds. In Malwa the capsules are ready in March or April. A somewhat different instrument is used to collect the juice, and from time to time this is dipped in linseed oil to prevent the juice adhering. Owing to the heavy dews the juice in India is much more moist than in Asia Minor (*ibid.* [i.] 11, 209).

When freshly collected the juice consists of a wet granular mass of a pinkish colour, from which there collects in the bottom of the vessel a dark coffee-coloured acid liquid 'pasewa' or 'pussewah.' More of this liquid is separated by draining, and the opium is then carefully dried by exposure to the air, but protected from the rays of the sun. The drying is continued some three or four weeks until the moisture is reduced to 30 p.c., the amount allowed by the Bengal regulations. In this state it arrives at the Government factory, where it is examined physically and chemically, and if satisfactory is admitted. In the factory great care is taken, by mixing low and high quality opiums, to send out a uniform product. It is manipulated into balls, and covered with poppy petals, which have been dried carefully. The petals are made to adhere together into a sort of shell by means of a liquid called 'lewa' or 'lewah,' made partly of opium and partly of 'pasewa.' The spherical cakes, which have a diameter of about six inches, and are not unlike in appearance a 24 lb. shot, are rolled in poppy 'trash,' powdered stalks, capsules, and leaves, put into earthenware moulds and exposed to the sun. If blisters form, the cake shells are opened, the gas allowed to escape and then tightly closed again. After three days, about the end of July, the cakes are put into frames and exposed to the air. There they remain, with constant watching, until October, when they are packed in chests, which contain wooden compartments for 40 cakes, and the interstices are loosely filled with poppy 'trash.' The chests, which contain 160 lbs., are then ready for exportation to China (Eatwell).

That which is consumed in India, 'abkari' opium, is prepared somewhat differently. It is dried by exposure to the sun until it contains only 10 p.c. of moisture, in which condition it admits of being moulded like wax. It is made into square bricks about 2 lbs. in weight, wrapped in oiled paper and packed in boxes furnished with suitable compartments. Except that the aroma is not quite so good, 'abkari' opium is equal in quality to that prepared for China (Eatwell, Pharm. J. [i.] 11, 269, 306, 359).

The opium of Malwa and other native districts is not so uniform in quality as that of the Government factories. Malwa opium contains only about 5 p.c. of moisture, and it is sent out in bricks or rounded masses which are not incased in poppy petals.

The percentage of morphine in Indian opium is much less than that found in the opium of Asia Minor. It is remarkable that a superior product in this respect has not been obtained to supply the English market, especially in view of the decreasing trade between India and China. Benares opium in 1845–9 contained 2·2 to 3·2 p.c. of morphine (Eatwell). Specimens of Patna garden opium, prepared especially for medicine, yielded 8·6 p.c. (Flück. a. Hanb.), 7·7 p.c. (Guibourt), 9·5 p.c. of hydrochloride (Christison). Specimens from the India Museum gave the following percentages of morphine: 'Khandesh,' 6·1 p.c.; 'medical opium,' 1852–3, part of a brick, 4·3 p.c.; 'garden Behar,' 4·6 p.c.; 'Abkari provision,' 'Patna,' 3·5 p.c.; 'Sind,' 3·8 p.c.; 'Hyderabad,' 3·2 p.c.; and 'Malwa,' 6·1 p.c. (Flück. a. Hanb.). Three specimens of Malwa opium examined by W. D. Howard contained 4·8 p.c., 6·0 p.c., and 9 p.c. of morphine (Flück. a. Hanb.).

Small quantities of morphine salts sometimes reach this country from India. They are made at the Government laboratories at Ghazipur from opium which has been confiscated on account of adulteration, and are not likely to become an important article of commerce (J. Soc. Chem. Ind. 1889, 917).

China. The Chinese consume a good deal of the opium exported from India, Asia Minor, and Persia, but not so much as formerly owing to the enormous development of the production in China, and this quantity, in accordance with the policy of the Chinese Government, will become less and less until the use of opium for smoking is abandoned altogether. It is not possible to estimate the amount produced in China, but some idea of the enormous increase may be gathered from consular and other reports. The various attempts of the Chinese Government to prohibit the manufacture of opium have had little effect. It was about 1830 that it began to be produced in notable quantities. In 1869, in a Report on the Trade of Hankow, addressed to the inspector-general of customs at Peking, the annual yield of the three provinces Yunnan, Kweichow, and Szechuen, was estimated at 41,000 peculs. In the same year it was reported that two-thirds of Szechuen and one-third of Yunnan was devoted to the poppy (Calcutta Blue Book, 205). In 1882 the annual production in the south-west of China, chiefly the provinces of Szechuen and Yunnan, was estimated at over 200,000 peculs, or more than twice the whole importation from India (Pharm. J. [iii.] 13, 225; *cf.* J. Soc. Chem. Ind. 1890, 74). In 1885 the imports of Indian opium in Manchuria had fallen to only 5 p.c. of what they were in 1866, its place being taken entirely by the native drug (Pharm. J. [iii.] 18, 280). In 1887 the district of Wenchow was occupied almost entirely in the production of opium. The country, viewed from a hill-top, was, in many places, one vast brilliant mass of poppy, with here and there a patch of green (J. Soc. Chem. Ind. 1888, 409). The consul at Niew Chang, in Manchuria, reports in 1889 that, although twenty years before 2,635 peculs of Indian opium supplied the whole province, at that time the port of Yingtzu alone consumed 3744 peculs annually. This enormous demand was being met almost entirely by the native drug.

Opium is cultivated chiefly in Szechuen, Yunnan, and Kweichow, to a less extent in Shanse, Shense, and Shantung, also in eastern Mongolia, and in Manchuria. The development of the poppy cultivation has been so great in many parts of China that it has seriously interfered with the supply of cereals. For this reason, since the famine, it has been prohibited in Shense, Honan, and Chihli. In Kwangtung the soil and climate are not suitable, and in Fuhkeen the production of sugar is equally or more remunerative (Holmes). In Szechuen, the poppy is a winter crop, and may be gathered in time to allow rice to be planted, and thus not interfere with the summer produce. The yield of opium is about 22 lbs. to the acre. Every part of the plant has a use, if only for manure, and thus the total return amounts to about double that of cereals. As soon as the summer crop is reaped, the soil is prepared and manured with night-soil. The seeds are sown in December, in drills 1½ foot apart, the white poppy being the most commonly cultivated in the low grounds. After a month, when the plants are a few inches high, the rows are thinned and banked up with earth. In March or April the flowering takes place, and at this time the roots are again well manured with night-soil. The capsules are slit in April or May (Pharm. J. [iii.] 13, 225). According to Thorel, the scarification and collection is precisely the same as that carried on in India. Some Szechuen specimens seem to have been collected with the use of oil as in Malwa (Flück. a. Hanb.).

Yunnan and Szechuen opium is made into flat cakes and wrapped in white paper. It is darker and softer than that of Persia, which it resembles. Chekeang is a treacly extract sold in 2 to 4 lb. jars. The product of Shense was supposed to resemble in flavour the highly-prized Patna opium. Yunnan ranks next and then Szechuen (Holmes). A specimen of Chinese opium, examined by Jamieson, contained:—Moisture, 18 p.c.; morphine, 5·9 p.c. (or 7·2 p.c. in the dried drug); narcotine, 7·5 p.c.; ash, 7·5 p.c. (Report on Trade of Hankow). Authentic specimens examined by Sheppard gave the following percentages of morphine in the dried opium:—Szechuen, 2·2; Kweichow, 2·5; Yunnan, 4·1; Kansu, 5·1. Eatwell in Szechuen found 3·3 and in Kweichow 6·1. Sheppard found 5 to 14 p.c. of moisture and 36 to 53 p.c. of extract soluble in water (Flück. and Hanb.).

Mozambique and Algeria. In 1877 a Portuguese company was founded to commence the opium culture in Mozambique (Pharm. J. [iii.] 8, 1007; 10, 63, 13, 445). In 1882, according to Guyot, some three hundred labourers were employed in cultivating Zambesi opium between the Muto and Quaqua rivers. The yield compares favourably with that in India. The product is said to be largely admixed with foreign substances before being made into 500 gram balls, which are packed in boxes containing poppy 'trash,' and covered with indigenous cotton (Compt. rend. 95, 798). These balls are sometimes seen in the English market. According to more recent advices, the company has been obliged to go into liquidation, and the cultivation has been abandoned (Pharm. J. [iii.] 21, 87). Opium has been collected in Algeria in small quantity since 1828 (*ibid.* [i.] 15, 348). A dried specimen examined by Guibourt contained 12·1 p.c. of morphine (Jahrb. 1862, 374; Aubergier found 1·5 to 17·8 p.c. (Ann. Chim. Phys. [iii.] 20, 303).

Australia. The production of opium commenced about 1868, and the first specimen reached this country from Victoria, and was examined by Morson in 1869. It contained, according to Hood, 2 p.c. of morphine and 8 p.c. of narcotine (Pharm. J. [iii.] 1, 272). Specimens containing 4·2 to 7·1 p.c. of morphine were sent to England in 1870. They were produced in the village of Sunbury, near Melbourne (Hood). About this time the cultivation was commenced in Gippsland, and opium containing 9 p.c. of morphine, 4 p.c. of narcotine, and 6 p.c. of meconic acid, was obtained (Ward, *ibid.* [iii.] 1, 543). The Toowoomba district in Queensland also furnished some good specimens (*ibid.* [iii.] 1, 972).

The chief part of colonial opium in the Melbourne market comes from the Bacchus Marsh district, where the cultivation has been carried on for years. The sowing takes place at three periods, about the first week in

May, the second or third week in June, and the latter part of July. By this means parts of the crop mature in succession. The average yield is 15 to 25 lbs. to the acre, but in a good season as much as 30 to 40 lbs. are obtained. In Europe the average yield to the acre is 25 lbs., and in India 30 to 40 lbs. When the capsules are ready, two incisions are made horizontally, half-way round, and the juice which exudes is collected the next morning. A few days later other incisions are made, until the capsule is exhausted. The opium is manipulated into balls and carefully dried. In quality it approximates to the product of Asia Minor. A specimen gave 11·5 of morphine from the dry drug. Another from Queensland contained 9·8 p.c. (Matthews, Austral. J. Pharm. Nov. 1887).

Europe and North America. Attempts have been made in most European countries, in Greece, Italy, Spain, France, Switzerland, Germany, England, and Sweden, to cultivate opium, and the results have shown that, providing the soil selected is suitable, and the rainfall not excessive, it is possible, in all these countries, to produce opium equal to that of Asia Minor. The most important European experiments have been conducted in France. A product called 'affium' has been made at Clermont-Ferrand, which is said to contain uniformly 10 p.c. of morphine; but it has not become an important article of trade (Flück. a. Hanb.; Aubergier, Pharm. J. [iii.] 15, 693). Some interesting investigations have been made in the neighbourhood of Amiens, where specimens of dry opium were produced containing 16 and 20 and still higher percentages of morphine. It was observed by Descharme that the morphine diminished when the juice was slowly dried, and the peculiar odour of the drug is ascribed to a species of fermentation (J. Pharm. Chim. [iv.] 6, 222). Guibourt found the percentage of morphine in French opium to vary from 12·1 to 22·8, the latter being the highest proportion of morphine ever recorded (*ibid.* [iii.] 41, 184, 201). Other analyses of French opium give 17·6 p.c. (Descharme, Compt. rend. 40, 34); 17·5 (Chevallier, Flück. a. Hanb.); 8·2 (Roux, J. 1855, 717); 11·1 to 11·9 (Petermann, Jahrb. 1866, 704). German opium from Erfurt contained 16·6 and 20 p.c. (Biltz, Gm. 16, 415); from Wurtemberg, 12 to 15 p.c. (Hesse, Flück. a. Hanb.); and from Silesia, 9 to 10 p.c. (Hesse).

Experiments have been carried out on the cultivation of poppies for opium production in the gardens of the Pharmaceutical Institute of the University of Berlin. The amount of opium obtainable from poppies in that latitude is satisfactory; but the cost of collecting it proves to be too high (Thoms, Zeitsch. angew. Chem. 21, 2208). The poppy is rarely grown in Russia, although there are many districts with a suitable soil and climate. Samples of Russian opium from the Ssemiretschinsky district contained about 7·5 p.c. of morphine (Goldberg, Chem. Zeit. 25, Rep. 67).

Experiments in North America lead to the same results as in Europe. Specimens from Vermont contained 15·75 p.c. of morphine (Procter, Amer. J. Pharm. [iii.] 18, 124); from Illinois, 8·75 p.c. (Kennedy, *ibid.* [iv.] 1, 6); and from California, 7·75 p.c. (Maisch, *ibid.* [iv.] 3, 103).

Chemical constituents. The important chemical constituents of opium may be divided into alkaloids, neutral compounds, and acids. For full particulars of all of these see VEGETO-ALKALOIDS. There are in opium some twenty alkaloids:—(1) *Morphine*, $C_{17}H_{19}NO_3,H_2O$, the most important constituent of opium. Its discovery and the proportion in which it occurs in opium have been already given. It is crystalline and forms crystalline salts. (2) *Codeine*, morphine methyl ether, $C_{18}H_{21}NO_3,H_2O$, was discovered in opium by Robiquet (Annalen, 5, 106) and may be prepared by the action of methyl iodide on morphine. It melts at 155°. Percentage in Smyrna, French, or Indian opium, 0·2 to 0·4 (Pharm. J. [ii.] 7, 183). (3) *Hydrocotarnine* $C_{12}H_{15}NO_3,\frac{1}{2}H_2O$ occurs in small proportion in opium (Hesse, Annalen Suppl. 8, 326) and is formed by the oxidation of narcotine (Beckett and Wright, Chem. Soc. Trans. 28, 577). (4) *Thebaïne*, $C_{19}H_{21}NO_3$ was isolated by Thiboumèry (Pelletier, J. Pharm. Chim. [ii.] 21, 569). Turkish opium contains about 1 p.c. (5) *Pseudomorphine* $C_{34}H_{36}N_2O_6,3H_2O$ (Pelletier and Thiboumèry, *ibid.* [ii.] 21, 575) occurs in opium to the extent of 0·02 p.c. or even less. (6) *Codamine*, $C_{20}H_{25}NO_4$; (7) *Laudanine*, $C_{20}H_{25}NO_4$; (8) *Laudanosine*, $C_{21}H_{27}NO_4$, and (9) *Meconidine*, $C_{21}H_{23}NO_4$, which exist in opium in minute quantities, were discovered by Hesse (Annalen, 153, 47, 56; Suppl. 8, 272, 280, 321). (10) *Papaverine*, $C_{20}H_{21}NO_4$, was discovered by Merck in opium (Annalen, 66, 125; 73, 50). It exists to the extent of about 1 p.c. (11) *Lanthopine*, $C_{23}H_{25}NO_4$ (Hesse, *ibid.* 153, 57; Suppl. 8, 271). (12) *Protopine* $C_{20}H_{19}NO_5$ (Hesse, *ibid.* Suppl. 8, 318) and (13) *Cryptopine*, $C_{21}H_{23}NO_5$ (T. and H. Smith, Pharm. J. [ii.] 8, 595, 716) are found in opium in very small proportions. (14) *Narcotine*, $C_{22}H_{23}NO_7$. The discovery of this base has been referred to already. It exists free in opium and may be extracted by benzene in which morphine is insoluble. Turkish opium usually contains 1 to 2 p.c., but East Indian and Persian opium often contain much more narcotine than morphine. In some specimens the proportion reaches 10 p.c. It is crystalline, melts at 176° and forms salts with difficulty. (15) *Rhœadine* $C_{21}H_{21}NO_6$, a base found in the *Papaver Rhœas* (Linn.), probably occurs in opium in minute quantity (Hesse, Annalen, 140, 145). (16) *Oxynarcotine*, $C_{22}H_{23}NO_8$ (Beckett and Wright, Chem. Soc. Trans. 29, 461). (17) *Narceïne*, $C_{23}H_{27}NO_8,3H_2O$, was discovered by Pelletier in opium in which it is found to the extent of 0·02 to 0·1 or even 0·7 p.c. (Ann. Chim. Phys. [ii.] 1, 262). It consists of long colourless prisms which lose water at 100° and melt at 145° (Hesse, Ber. 7, 105). (18) *Gnoscopine* (*dl-narcotine*), $C_{22}H_{23}NO_7$ (T. and H. Smith, Pharm. J. [iii.] 9, 82; 52, 794). (19) *Tritopine*, $C_{42}H_{54}N_2O_7$ (Kauder, Arch. Pharm. 228, 419). (20) *Papaverosine*, a base found in poppy capsules by Deschamps (J. 1864, 446) but not hitherto detected in opium. (21) *Laudanidine*, $C_{20}H_{25}NO_4$ (Hesse, Annalen, 282, 208). (22) *Xanthaline* or *Papaveraldine*, $C_{20}H_{19}O_5N$ (T. and H. Smith, Pharm. J. 52, 793; Dobson and Perkin, Chem. Soc. Trans.

99, 135). (23) *Hydroxycodeme*, $C_{18}H_{21}O_4N$ (Dobbie and Lauder, Chem. Soc. Proc. 1910, 339). With the exception of morphine and narcotine the remaining bases do not occur in opium to a greater extent together than 2 p.c. and generally not more than 1 p.c.

The neutral compounds are:—(1) *Meconin*, $C_{10}H_{10}O_4$, discovered by Dublanc (Ann. Chim. Phys. [ii.] 49, 5), but more completely studied by Couerbe (Annalen, 5, 180). It may be obtained by the oxidation of narcotine (Anderson, *ibid.* 86, 191; 98, 44) and is formed in other reactions. It is an inner anhydride

$$C_6H_2(OMe)_2\underline{CH_2{\cdot}COO}$$

(Hessert, Ber. 11, 257). (2) *Meconoisin*, $C_8H_{10}O_2$ or perhaps $C_6H_2(Me)_2(OH)_2$. It is crystalline, melts at 88°, and was found by T. and H. Smith in the mother-liquor from the preparation of meconin (Pharm. J. [iii.] 8, 981).

The discovery of *Meconic acid* $C_7H_4O_7,3H_2O$ has already been mentioned. It is a tribasic acid forming primary, secondary, and tertiary salts. Heated to 100° it loses its water of crystallisation, and at 120° to 200° it breaks up into carbon dioxide and *comenic acid* $C_6H_4O_5$, and at a higher temperature into another molecule of carbon dioxide and *pyromeconic acid*, $C_5H_4O_3$. Meconic acid occurs in opium to the extent of 3 to 5 p.c. in combination with morphine, and perhaps with other bases. The 'bolactic acid' of T. and H. Smith (Pharm. J. [ii.] 7, 50) has been shown by Stenhouse (Watts' Dict. 1st ed. 5, 759) and Buchanan (Ber. 3, 182) to be identical with lactic acid. Turkish opium contains, according to T. and H. Smith, 2 p.c., but it is probably not an original constituent of the poppy-juice (Flück. a. Hanb.).

The less important constituents of opium represent three-fourths of its weight. *Water* exists to a very variable extent. Turkish opium contains on an average 12·5 p.c. The Bengal opium sent to China is made to contain uniformly 30 p.c. About 50 p.c. of opium is composed of a *gum*, having properties distinct from gum arabic, *pectin*, *albumen*, and fragments of capsules. *Sugar* is present in French opium to the extent of 6·5 to 8·0 p.c., and is said to be uncrystallisable. Of that part of Turkish opium insoluble in water, 6 to 10 p.c. is composed of *wax*, pectin, and insoluble calcium salts. The wax, which exists in the juice as an emulsion, is a mixture of *cerotyl palmitate*, and *cerotyl cerotate* (Hesse, Ber. 3, 637). Vermont opium contained 11 p.c. of *caoutchouc* (Procter). The *colouring matter* and a *pungent volatile substance*, which is removed by benzene or acetone, have not been examined. Opium leaves 4 to 8 p.c. of *ash* consisting chiefly of sulphate and phosphate of calcium and magnesium. Poppy-juice contains no starch or tannin. The presence of these substances in opium is therefore an indication of adulteration.

Microscopic examination of opium and the constituents extracted by solvents (Deane and Brady, Pharm. J. [ii.] 6, 234; 7, 183). Examples of analyses: Persian opium (W. D. Howard, *ibid.* [iii.] 6, 721); Australian opium (Ward, *ibid.* [iii.] 1, 543; Matthews, Austral. J. Pharm. Nov. 1887); Vermont opium (Procter, Amer. J. Pharm. [iii.] 18, 124); Flückiger (Jahr. 1869, 797; Pharm. J. [ii.] 10, 208); Indian and Chinese opium (Browne, *ibid.* 84, 452; van Itallie and Kerbosch, Arch. Pharm. 248, 609).

For determination of morphine in opium, *v.* Kebler (J. Soc. Chem. Ind. 14, 464); Dott (*ibid.* 15, 91); Gordin and Prescott (Arch. Pharm. 237, 380); Dowzard (Pharm. J. 71, 909); Schidrowitz (Analyst, 29, 144); and for determination of narcotine and codeine, van der Wielin (Pharm. Zeit. 48, 267); Caspara (J. Pharm. Chim. 20, 458); Andrews (Analyst, 36, 489).

Physiological action and uses.—Opium is without doubt the most important remedy available for use in medicine. Its action on man is chiefly on the brain, producing sleep. In doses of a grain or less, a stage of slight excitement supervenes during which the individual can control his energies. In 1 to 2 grain doses the stage of excitement is short and is succeeded by deep sleep, after which there is nausea and headache. If large doses of 3 grains or more be administered the excitement is very short and is followed by sleep which becomes more and more comatose until the patient cannot be aroused. If death takes place the respiration ceases first. Opium is used for the alleviation of pain, either generally or locally, for the production of sleep, or for reducing the irritation of various organs. Its special applications in the treatment of disease are almost endless (*cf.* Brunton, Pharm. Therapeut., 1887, 852).

The action of opium in stimulating and then depressing gives rise to the desire to repeat the dose. In this way the habit of 'opium eating' is contracted. The worst effects of opium are thus obtained. It deranges the nervous system, and impairs the intellectual and moral and finally also the physical powers. De Quincey's description of his own experience is well known.

But by far the largest quantity of opium is used for smoking. The habit is believed to have originated in Persia, but it is in China, where it prevails to the greatest extent at the present day, where, indeed, its use appears to be almost as widely diffused as the use of tobacco in Europe. For smoking the opium undergoes a process of preparation which is a business in itself. In Hong Kong, according to McCallum, the opium is extracted by boiling with water and the clear solution is evaporated until it attains the consistence of treacle (Pharm. J. [iii.] 11, 229; 12, 446). The Chinese in California first put the opium through a series of roasting processes which are said to destroy its stickiness and render it more easily extracted by boiling with water (Calvert, *ibid.* [iii.] 120, 148). The Chinese recognise four varieties of opium:—(1) Raw opium; (2) Prepared opium, the treacly extract described; (3) Opium 'dross,' the scrapings of the opium pipe, which are said to be strong, hot, of inferior flavour; (4) Opium 'dirt,' the exhausted marc after extraction with water (McCallum).

The whole operation of opium-smoking is described in a letter which accompanied an opium-smoker's set of apparatus in 1882 from Canton to Kew. The pipe has a flat bowl made of metal with a very small opening. A drop of the soft opium is taken on the point of a 'dipper' and dexterously roasted in the flame of a little lamp until with constant burning it has the appearance of burnt worsted. Then, first warming the bowl of the pipe, the drug, about the size of a hemp-seed, is placed about the opening in the bowl, the pipe taken in the mouth and the opium ignited. The smoke is partly swallowed or inhaled and partly exhaled by the mouth and nose. The preparation for smoking occupies 5 or 10 minutes, but the actual smoking only about 30 seconds (Sampson, *ibid.* [iii.] 11, 22).

The physiological action of opium smoked in this way is clearly quite different from what it is when taken in the stomach. It is noteworthy that those opiums most highly prized for smoking contain a small percentage of morphine. It would seem that, notwithstanding the serious view of the effects of opium-smoking taken by the Chinese Government and held by many Europeans, the habit is not more injurious than the use of other stimulants. Opium in the East seems to perform the same function that alcohol does in the West, and, as far as can be ascertained, with about the same good and bad effects (*cf.* Birdwood, Pharm. J. [iii.] 12, 500; Spence, *ibid.* [iii.] 13, 226; McCallum, *ibid.* [iii.] 14, 27; James, *ibid.* [iii.] 18, 280).

A. S.

OPOBALSAM *v.* Oleo-resins.

OPODELDOC. *Linimentum Saponato-camphoratum.* A solution of soap, camphor, and volatile oils in alcohol, used externally in rheumatism, sprains, &c.

OPOPANAX or **OPOPONAX** *v.* Gum-resins.

ORANGE. *Citrus Aurantium* (Linn.).

Many varieties are known, differing in size, shape, colour, flavour, and other respects. König gives as the average of a very large number of determinations—

Mean wt. of fruit in grams.	Percentage proportion of—		
	Rind	Flesh	Pips
188·4	27·8	71·0	1·2

The flesh contains—

Water	Protein	Invert sugar	Cane sugar	Citric acid	Ash
84·3	1·1	2·8	2·9	1·4	0·4

The juice contains—

Total extract	Invert sugar	Cane sugar	Citric acid	Protein	Ash
13·0	4·1	5·0	1·4	0·4	0·3

The following figures were obtained by Farnsteiner and Stüber (Zeitsch. Nahr. Genussm. 1904, 8, 603) from the examination of the juice of Valencia and Messina oranges :—

	Valencia oranges	Messina oranges
Sp.gr. at 15° . .	1·0464	1·0451
„ „ after boiling	1·0466	1·0455
Grams per 100 c.c.—		
Total solids, dried at 100°	10·92	10·85
Citric acid (anhydrous) .	1·79	1·47
Total sugar (as invert sugar) . .	7·65	7·86
Ash	0·52	0·52
Nitrogen	0·099	0·075
Polarisation in 200 mm. tube, direct . .	−0·11°	+2·45
Polarisation in 200 mm. tube, after inversion .	−3·16°	−3·66

The characteristic flavour of oranges is due to the sugar, free citric and malic acids, and essential oils which they contain. The last-mentioned is most abundant in the rind (*v.* Oils, essential). The non-protein nitrogenous matter of oranges consists chiefly of asparagine and glutamine (Scurti and de Plato, Chem. Zentr. 1908, ii. 16, 1370).

The fibrous, insoluble, inside portions of Japanese oranges were found to contain—

Water	Protein	Fat	Galactan	Pentosan	Cellulose	Ash
12·16	5·27	1·28	18·91	27·72	32·51	2·15

(Bahadur, Bull. Coll. Agr. Tokyo Imp. Univ. 1906, 7, 121). The leaves of the bitter orange (*Citrus vulgaris* [Risso]) contain stachydrine (Jahns, Ber. 1896, 29, 2065). Dried orange-peel, softened with acetic acid and boiled with water, yields about 8 or 9 p.c. of lævulose (Bauer, Landw. Versuchs-stat. 1894, 45, 298). H. I.

ORANGITE. An orange-coloured variety of the mineral thorite (*q.v.*), occurring as tetragonal crystals and irregular masses, occasionally a few ounces in weight, in the augite-syenite of southern Norway. It was described and named by C. Bergemann in 1851, and believed by him to contain a new element 'donarium.' The identity of the mineral with thorite has long been recognised.

L. J. S.

ORANGE, CHROME, *v.* Chromium.

ORANGE, CROCEÏN *v.* Azo- colouring matters.

ORANGE FLOWERS, OIL OF, *v.* Oils, essential.

ORANGE, GOLD *v.* Azo- colouring matters.

ORANGE LEAVES, OIL OF, *v.* Oils, essential.

ORANGE M; ORANGE, MANDARIN; ORANGE, METHYL; ORANGE, NAPHTHOL, *v.* Azo- colouring matters.

ORANGE OCHRE. *Burnt Roman ochre* *v.* Pigments.

ORANGE OIL *v.* Oils, essential.

ORANGE, PALATINE, *v.* Palatine orange.

ORANGE RUSSET. *Rubens madder* *v.* Pigments.

ORANGE, SALICYLIC, *v.* Salicylic Acid.

ORANGE YELLOW *v.* Azo- colouring matters.

ORCEÏN *v.* *Orcinol*, art. Phenol and its homologues.

ORCHELLA WEED *v.* Archil.

ORCHIDIN *v.* Synthetic drugs.

ORCHIL *v.* Archil.

ORCHIL SUBSTITUTE *v.* Azo- colouring matters.

ORCHIPIN *v.* Synthetic drugs.

ORCIN *v.* *Orcinol*, art. Phenol and its homologues.

ORCINOL *v.* Phenol and its homologues.

ORDEAL BEAN. *Calabar Bean, Physostigma, Eseré Nut* (*Fève de Calabar*, Fr.; *Kalabarbohne*, Ger.). The seeds of the *Physostigma venenosum* (Balfour), a climbing plant, inhabiting the banks of the Niger and Old Calabar rivers near their mouths, in Western Africa (*cf.* Bentl. a. Trim. 80, and, for an allied species, Holmes, Pharm. J. [iii.] 9, 912). The plant has a woody stem, and ascends to a height of fifty feet. The seeds are exceedingly poisonous, a property known to the natives in the neighbourhood of the Gulf of Guinea, by whom they are administered as an ordeal to be undergone in cases of suspected witchcraft. Daniel, about 1840, introduced ordeal bean into

Europe (N. Ed. Pharm. J. 40, 313), and its physiological action was examined by Christison (Pharm. J. 14, 470). It causes a marked contraction of the pupil of the eye, and on this account is much used in ophthalmic medicine. With regard to the antagonism between ordeal bean and belladonna, *v.* Bennett (Brit. Med. J. 1875, 464). It is given in cases of poisoning by strychnine, and generally in tetanus and chorea (*cf.* Flück. a. Hanb. 191).

The physiological activity of ordeal bean depends chiefly upon the presence of the alkaloid *physostigmine* or *eserine*, $C_{15}H_{21}N_3O_2$, discovered by Jobst and Hesse (Annalen, 129, 115). To obtain it, the seed is exhausted with alcohol, and the alcohol removed from the solution by distillation. The residue is mixed with sodium bicarbonate and extracted with ether. The ethereal solution is shaken with water containing sulphuric acid, and the acid solution of alkaloidal sulphate is treated with excess of sodium bicarbonate. Ether now extracts the physostigmine and yields it as a brittle varnish on evaporation (Hesse, Annalen, 139, 82). Petit shakes the last ethereal solution with water, containing just sufficient sulphuric acid to neutralise the alkaloid. In this way, after removal of the ether and evaporation, crystals are obtained of neutral sulphate of physostigmine (J. Pharm. Chim. [iv.] 14, 255).

Physostigmine is tasteless but exceedingly poisonous. It forms colourless or pinkish crystals which melt at 105°–106° (Petit and Polonowsky, J. Pharm. Chim. [v.] 29, 55). It is soluble in alcohol, ether, benzene, carbon disulphide, and chloroform; but is only sparingly soluble in water. It oxidises readily, especially when moist, at 100°, a compound being formed which gives a red colour with acids. Bleaching powder also gives a red colour reaction with physostigmine. The alkaloid in solution precipitates ferric chloride, and combines with acids to form salts. Most alkaloidal reagents precipitate physostigmine. The compound with potassiomercuric iodide $C_{15}H_{21}N_3O_2,KI,HgI_2$ is white, insoluble in water, but soluble in alcohol, from which it may be obtained in crystals which melt at 70° (Hesse). When the alkaloid is neutralised with dilute sulphuric acid, an excess of ammonia added, and the mixture evaporated to dryness, a magnificent blue residue remains. The blue compound is soluble in water and alcohol, and may be crystallised from these solvents in elongated prisms. If to a solution of the base in water ammonia be added and the mixture be evaporated at 100° a bluish residue remains, which on the addition of an acid becomes beautifully dichroic blue and red (Petit, Compt. rend. 72, 569; J. C. Umney, Pharm. J. [iii.] 20, 1061). When heated with aqueous alkalis in presence of air, eserine first yields *rubreserine*, $C_{18}H_{16}N_2O_2$, which crystallises in red needles, but which is gradually converted into *eserine blue.* This is a true dye, colouring silk and wool without mordants (Ehrenburg, Chem. Zentr. 1894, ii. 439). A list of colour reactions of eserine is given by Reichard (Pharm. Zentr. 50, 375).

According to Harnack and Witkowsky (Pharm. J. [iii.] 8, 2), ordeal bean contains a second alkaloid, *calabarine*, which differs in its solubilities and its physiological action from physostigmine; indeed, it appears in the latter respect to resemble strychnine. Another compound, *phytosterol*, has been isolated by Hesse (Annalen, 192, 175). It consists of brilliant tabular crystals, which melt at 132°–133°, and is extracted from the seed by light petroleum (*cf.* MacEwan, Pharm. J. [iii.] 17, 641). Windaus and Hauth (Ber. 39, 3478) show that this product is not a single substance. By suitable treatment it can be separated into *sitosterol* $C_{27}H_{46}O$, m.p. 136°–137°, identical with the compound obtained from germinating wheat by Burian (Monatsh. 18, 551) and *stigmasterol* $C_{30}H_{48}O,H_2O$, m.p. 170°. By acting on physostigmine with reducing agents, Eber (Pharm. J. [iii.] 19, 161, 345) has obtained a compound *eseridine* $C_{15}H_{23}N_3O_3$, which is said also to be a constituent of the seed (Böhringer und Söhne, Pharm. Post, 21, 663). It liberates iodine from hydriodic acid. By treatment with acids it is reconvertible into physostigmine. Eseridine is distinguished from eserine by not yielding rubreserine under the influence of alkalis and air. A further alkaloid has been isolated by Ehrenberg (*l.c.*), *eseramine* $C_{16}H_{25}N_4O_3$, which crystallises from alcohol in slender white needles. It is not identical with Harnack's calabarine and doubts are expressed whether calabarine exists as such in the beans. Ogui (Apoth. Zeit. 19, 981) has also described another alkaloid, iso*physostigmine*, isomeric with physostigmine, but Salway (Chem. Soc. Trans. 99, 2148) obtained no evidence of the presence of this alkaloid or of eseridine. Salway finds that physostigmine can be obtained in two interconvertible modifications, m.p. 86°–87° and 105°–106° respectively, and he has also isolated a new alkaloid, *physovenine* $C_{14}H_{18}O_3N_2$, m.p. 123°, which, like physostigmine, produces a powerful myotic effect on the pupil of the eye, in addition to *calabarol* $C_{23}H_{36}O_4$, m.p. 245°, a new dihydric alcohol, and *trifolianol* $C_{21}H_{36}O_4$, a dihydric alcohol previously isolated from red clover flowers.

For estimation of alkaloids in ordeal bean by means of Mayer's reagent *v.* Masing (Arch. Pharm. 1877, 310). Gravimetric methods (Gibson, Pharm. J. [iii.] 15, 593; MacEwan, *ibid.* [iii.] 15, 594; 17, 642). A. S.

OREIDE. An alloy of a brilliant-yellow colour, resembling gold, made by taking copper 100, zinc 17, magnesia 6, sal ammoniac 3·6, lime 1·80, and tartar 9. The copper is melted and the other materials are added in small portions at a time, and the fused mass is skimmed and kept melted for about half an hour. The alloy has a fine grain, is malleable, takes a most brilliant polish, and if it tarnishes its lustre is restored by acidulated water.

ORELLIN. A yellow colouring matter contained in annatto, which is derived from the fruit capsules of *Bixa Orellana* (Linn.). Soluble in water and alcohol.

ORICHALCUM. A form of brass in use among the ancient Greeks and Romans.

ORIENTAL EMERALD, ORIENTAL TOPAZ *v.* Corundum.

ORIENTAL ALABASTER *v.* Onyx-marble.

ORIGANUM OIL *v.* Oils, essential.

ORIOL YELLOW *v.* Primuline and its Derivatives.

ORMOLU *v.* Mosaic gold.

ORNITHINE, *αδ-diaminovaleric acid*

$$NH_2[CH_2]_3CH(NH_2)CO_2H,$$

was first prepared by Jaffé (Ber. 1877, 10, 1926; 1878, 11, 40) from its dibenzoyl derivative *ornithuric acid*, found in the excrement of birds that had been fed with benzoic acid. It occurs among the products of alkali hydrolysis of certain proteins, probably arising from arginine by a further hydrolysis (Kossel and Weiss, Zeitsch. physiol. Chem. 1909, 59, 492; 60, 311; 1910, 68, 160); and it can also be obtained from arginine by the action of *arginase* (*q.v.*); or by hydrolysis with barium hydroxide (Schulze and Winterstein, Ber. 1897, 30, 2879).

Jaffé (*l.c.*) showed that ornithine was a diaminovaleric acid, the position of the two amino groups being determined by Ellinger (Ber. 1898, 31, 3183), who obtained *putrescine* (tetramethylenediamine. Udransky and Baumann, *ibid.* 1888, 21, 2938) and carbon dioxide by the action of putrefying pancreas on ornithine.

$$\underset{\text{Ornithuric acid.}}{COPh{\cdot}NH[CH_2]_3CH(NH{\cdot}COPh)CO_2H}$$

$$\rightarrow \underset{\text{Ornithine.}}{NH_2[CH_2]_3CH(NH_2)CO_2H} \rightarrow \underset{\text{Putrescine.}}{NH_2[CH_2]_4NH_2}$$

Ornithine has been synthesised by Fischer (Ber. 1901, 24, 454) by the following series of reactions:—

Ethyl-γ-phthalimidopropylmalonate

$$C_6H_4[CO]_2N{\cdot}[CH_2]_3{\cdot}CH(CO_2Et)_2$$

obtained from potassium phthalimide, propylene bromide, and ethyl sodiomalonate, yields ethyl γ-phthalimidopropylbromomalonate on bromination; this is converted by hydrolysis with loss of carbon dioxide into δ-phthalimido-α-bromovaleric acid $C_6H_4[CO]_2N[CH_2]_3CHBr(CO_2H)$, which, on treatment with ammonia and subsequent hydrolysis, yields αδ-diaminovaleric acid or inactive ornithine. A similar synthesis has been effected by Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); and a synthesis from benzoylpiperidine is described by Fischer and Zemplén (Ber. 1909, 42, 1022).

Ornithine is not crystalline, but forms crystalline salts; it is readily soluble in water, forming an alkaline solution; it contains an asymmetric carbon atom and derivatives of the dextro, lævo, and racemic varieties are described.

d-**Ornithine.** The ornithine hydrochloride obtained by hydrolysis of naturally occurring ornithuric acid has $[\alpha]_D + 15{\cdot}64°$ to $16{\cdot}8°$ (Schulze and Winterstein, Zeitsch. physiol. Chem. 1901, 34, 128), and *d*-ornithine is also obtained by the hydrolysis of *d*-arginine with barium hydroxide.

Salts. Hydrochlorides $C_5H_{12}O_2N_2,2HCl$ and $C_5H_{12}O_2N_2,HCl$; platinichloride

$$C_5H_{12}O_2N_2,H_2PtCl_6;$$

nitrate $C_5H_{12}O_2N_2,HNO_3$;

oxalate $3C_5H_{12}O_2N_2,2C_2H_2O_4$;

acetate, m.p. 161°–162°;

picrate $C_5H_{12}O_2N_2,C_6H_3O_7N_3$

(Schulze and Winterstein); or with $1H_2O$, m.p. 198°–199° (Riesser); or m.p. 203°–204° (Kossel and Weiss).

Acyl derivatives. The hydantoin $C_{19}H_{20}O_3N_4$, m.p. 191°–192°; the β-naphthalenesulphone

$$C_5H_{10}O_2N_2(SO_2{\cdot}C_{10}H_7)_2,$$

m.p. 189°; the monobenzoyl $C_{12}H_{16}O_3N_2$, m.p. 225°–240°; the dibenzoyl (*d-ornithuric acid*)

$$PhCO{\cdot}NH[CH_2]CH(CO_2H)NH{\cdot}COPh,$$

m.p. 184°–185°, $[\alpha]_D + 9{\cdot}2°$ to $9{\cdot}3°$ in 10 p.c. solution of sodium salt, $+8{\cdot}5°$ in 20 p.c. solution; brucine *d*-ornithurate

$$C_{19}H_{20}O_4N_2{\cdot}C_{23}H_{26}O_4N_2,H_2O,$$

m.p. 135°–136°, separates from a solution of brucine in racemic ornithuric acid.

l-**Ornithine.** *Acyl derivatives.* The dibenzoyl (*l*-ornithuric acid) $C_{19}H_{20}O_4N_2$, from *dl*-ornithuric acid by fractional crystallisation of the cinchonine salt; m.p. 188°–189°, $[\alpha]_D - 9{\cdot}22°$ in 10 p.c. solution of the sodium salt; cinchonine *l*-ornithurate $C_{19}H_{20}O_4N_2{\cdot}C_{19}H_{22}ON_2,H_2O$, the anhydrous salt has m.p. 154°–155° (corr.); monobenzoyl $C_{12}H_{16}O_3N_2$, m.p. 240°; the phenyl*iso*cyanate, m.p. 189°–190° (corr.); the hydantoin, m.p. 191° (corr.).

dl-**Ornithine,** obtained by the putrefactive hydrolysis of arginine carbonate (Ackermann, Zeitsch. physiol. Chem. 1908, 56, 305); by hydrolysis of clupeine sulphate with barium hydroxide (Kossel and Weiss, *ibid.* 1909, 59, 492; 60, 311); is also prepared by any of the synthetic methods described above.

Salts. Hydrochloride $C_5H_{12}O_2N_2,HCl$, m.p. 215°; aurichloride $C_5H_{12}O_2N_2(HAuCl_4)_2,H_2O$, decomposes at 173°–175°; platinichloride $C_5H_{12}O_2N_2{\cdot}H_2PtCl_6$; sulphate

$$(C_5H_{12}O_2N_2)_2H_2SO_4,$$

m.p. 213°; nitrate $C_5H_{12}O_2N_2{\cdot}HNO_3$, m.p. 183°; oxalate $(C_5H_{12}O_2N_2)_2C_2H_2O_4$, m.p. 218°; carbonate; acetate $C_5H_{12}O_2N_2{\cdot}C_2H_4O_2$, m.p. 163°–164°; monopicrate $C_5H_{12}O_2N_2{\cdot}C_6H_3O_7N_3$, m.p. 170°, triclinic system,

$$a : b : c = 0{\cdot}6962 : 1 : 0{\cdot}6301,$$

$\alpha = 93°\ 10'$, $\beta = 100°\ 55'$, $\gamma = 81°\ 19'$; dipicrate, $C_5H_{12}O_2N_2(C_6H_3O_7N_3)_2,2\frac{1}{2}H_2O$, m.p. 183°–184°; picrolonate $C_5H_{12}O_2N_2{\cdot}C_{10}H_8O_5N_4,1\frac{1}{2}H_2O$, m.p. 220°–221°. *Double salts,* with cupric sulphate $(C_5H_{12}O_2N_2)_2CuSO_4,H_2O$. m.p. 204°–205°; with cupric nitrate $(C_5H_{12}O_2N_2)_2Cu(NO_3)_2,\frac{1}{2}H_2O$, m.p. 167°–168°; with silver nitrate

$$C_5H_{12}O_2N_2{\cdot}HNO_3{\cdot}AgNO_3,$$

m.p. 175°.

Acyl derivatives. The phenyl*iso*cyanate, m.p. 192°; the hydantoin, m.p. 194°–195°; the β-naphthalenesulphone $C_5H_{10}O_2N_2(C_{10}H_7SO_2)$, m.p. 195°–196°; the δ-monobenzoyl

$$PhCO{\cdot}NH[CH_2]_3CH(NH_2)CO_2H,$$

m.p. 260°, or 285°–288° on the Maquenne block; the δ-*m*-nitrobenzoyl $C_{12}H_{15}O_5N_3$, m.p. 250°; the α-monobenzoyl

$$NH_2[CH_2]_3CH(NH{\cdot}COPh)CO_2H,$$

m.p. 264°–267°, on the Maquenne block; and the αδ-dibenzoyl (*dl*-ornithuric acid) $C_{19}H_{20}O_4N_2$, m.p. 187°–188°. M. A. W.

ORPHOL. Bismuth β-naphtholate, *v.* BISMUTH, ORGANIC COMPOUNDS OF; *also* SYNTHETIC DRUGS.

ORPIMENT (*Auripigmentum*). Native arsenic trisulphide, As_2S_3, crystallising in the orthorhombic system and isomorphous with stibnite (Sb_2S_3). Crystals are rare, the mineral usually occurring as laminated or scaly masses with a perfect cleavage parallel to the surface of the plates. The colour is lemon-yellow, and there is a pearly lustre on the cleavage surfaces. The mineral is very soft and sectile (H. $1\frac{1}{2}$–2), and the flakes are readily bent; sp.gr. 3·48. Orpiment occurs, usually in association with realgar (*q.v.*), in mineral-veins together with ores of silver, lead, &c., and also as nodules in beds of sandy clay. It is found at several places in Hungary, at Mercur in Utah, and in some abundance at Julamerk in Asiatic Turkey. Some hundreds of tons are exported annually from Shih-haung-Ch'ang in prov. Yunnan, China. The mineral is used as a pigment (King's yellow), but now mostly in the East; it is the auripigmentum (golden paint) of the ancients. Formerly it was also used in dyeing and calico-printing, and by tanners for removing hair from skins. L. J. S.

ORRIS ROOT is the peeled and dried rhizomes of *Iris florentina* (Linn.), *I. pallida* (Lam.), and *I. germanica* (Linn.). It is characterised by a pleasant aroma, and appears to be slightly detergent and antiseptic. It is employed in the preparation of violet-powder and dentifrices, and to a small extent as an ingredient of snuff.

ORSEILLINE *v.* AZO- COLOURING MATTERS.

ORSELLINIC ACID, $C_8H_8O_4,H_2O$, was first prepared by Stenhouse (Annalen, 68, 61), by digesting lecanoric acid with boiling baryta water, and can also be produced from erythrin in a similar manner. According to Hesse (*ibid.* 139, 35), the solution of erythrin in baryta water is heated on the steam bath until a sample of the product no longer yields a gelatinous precipitate when neutralised with hydrochloric acid. The liquid is then acidified, and the orsellinic acid, which separates on standing, is crystallised from alcohol or acetic acid.

Orsellinic acid crystallises from dilute acetic acid in needles with $1H_2O$. When heated, it melts at 176° with evolution of carbon dioxide and formation of orcin, and is evidently an orcin carboxylic acid.

Ethyl orsellinate $C_{10}H_{12}O_4$, colourless leaflets, m.p. 132°, is produced when erythrin is boiled for several hours with alcohol (Stenhouse, *l.c.*), and can be prepared in an identical manner from lecanoric acid (Schunck, Annalen, 54, 265).

Methyl orsellinate $C_9H_{10}O_4$ (Schunck, *l.c.*, and Stenhouse, *l.c.*), and iso*amyl orsellinate* $C_{13}H_{18}O_4$ (Stenhouse; Hesse, Annalen, 139, 37), m.p. 76° have also been obtained.

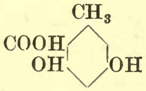
According to Henrich (Ber. 1904, 37, 1406), ethyl orsellinate in alkaline solution reacts with diazobenzene chloride, with formation of the disazobenzene derivative

$$C_6Me(OH)_2(C_6H_5N_2)_2COOEt,$$

red needles, m.p. 186°, and this, on reduction with stannous choride land hydrochloric acid, and further heating with hydrochloric acid at 160° gives diamino-orcin hydrochloride

$C_6HMe(OH)_2(NH_2)_2(Me:(NH_2)_2:(OH)_2=1:2:4:3:5$.

The constitution of orsellinic acid is therefore to be represented as follows:—



A. G. P.

ORTHITE, or Allanite. A complex rare-earth silicate belonging to the epidote group of minerals, and sometimes known as cerium-epidote. The general formula is $HR''R_3'''Si_3O_{13}$, where R''=Ca, Fe, and R'''=Al, Fe, Ce, La, Di, Y. The extreme values in the analyses tabulated by Dana are: SiO_2, 29·3–34·5; ThO_2, trace–3·5; Al_2O_3, 6·3–22·9; Fe_2O_3, 1·6–21·2; Ce_2O_3, 1·3–33·7; Di_2O_3, 2·9–24·0; La_2O_3, 0·2–8·1; Y_2O_3, 0·3–4·2; Er_2O_3, 0–2·0; H_2O, 0·3–14·6; also small amounts of manganous oxide, magnesia, and alkalis. Sp.gr. 3·5–4·2. The mineral crystallises in the monoclinic system, and has either a tabular or a long-prismatic habit. Compact masses and grains are also common. It is black or dark brown, opaque, and with a pitchy lustre on the bright sub-conchoidal fracture. On the exterior the material often presents a dull weathered appearance, the slender prismatic crystals looking rather like rusty nails. Tabular crystals from Greenland were described by T. Allan in 1808, and named allanite by T. Thomson in 1810. The later name orthite (from ὀρθός, straight) was given by J. J. Berzelius in 1818 to long prismatic crystals from Finbo in Sweden. Owing to difficulties of determination and to differences in composition and degree of hydration, several other minerals, now recognised as varieties of allanite, have been described as distinct species under special names. As an accessory constituent of crystalline rocks (gneiss, granite, andesite, &c.), allanite is not of uncommon occurrence in small amounts. It is well known in the granite at Criffel and several other places in Scotland, and in a quartz vein traversing granophyre in Merionethshire. It is found in some abundance in the felspar quarries of Sweden and Norway, and as large masses in gneiss at several American localities. Masses weighing over 300 pounds have been found at Barringer Hill in Llano Co., Texas, where, together with gadolinite, &c., it has been quarried for the supply of rare earths used in incandescent gas-lighting. L. J. S.

ORTHOCLASE. *Potash felspar v.* FELSPAR.

ORTHOFORM *v.* SALICYLIC ACID.

ORTOL. Trade name for a mixture of methyl-*o*-amidophenol and hydroquinone. Used as a photographic developer.

OSAZONES. A term given by E. Fischer to compounds of phenyl hydrazine with the sugars (*v.* HYDRAZONES and CARBOHYDRATES).

OSMIRIDIUM *v.* PLATINUM METALS.

OSMITOPSIS, OIL OF. *Osmitopsis asteriscoides* (Cass.), an aromatic plant of the order of *Compositæ*, growing in South Africa, yields a greenish-yellow oil of a burning taste and aromatic smell. Appears to be isomeric with borneol and oil of cajeput.

OSMIUM. Sym. Os. At.wt. 190·9.

This metal occurs in native platinum (*v.* PLATINUM), and especially in osmiridium. It differs from the other metals of the platinum group in forming a volatile tetroxide OsO_4, upon the production of which the separation of osmium from the other platinum metals, and especially from ruthenium, depends.

The osmiridium treated as described under IRIDIUM (*v.* also *infra*) yields the osmium in the form of this tetroxide, which may be reduced in hydrochloric acid solution by zinc or mercury (Berzelius, Ann. Chim. Phys. 1829, [ii.] 40, 258); with an alkaline formate; with hydrogen; a mixture of carbon mon- and dioxides or with carbon. In the latter case, the metal is obtained in a crystalline form, whilst by the other methods it is precipitated as a bluish powder (Doebereiner, Annalen, 1835, 14, 17; Deville and Debray, Compt. rend. 1876, 82, 1077).

The metal has also been obtained by the reduction of its ammoniacal or sulphur compounds (Berzelius, *l.c.*; 1829, [ii.] 42, 191; Fremy, *ibid.* 1855, [iii.] 44, 387; Schneider, Annalen, 1867, Suppl. 5, 261).

Osmium has a sp.gr. of 22·48 (Joly) (its sp.gr., however, depends on its state of division); and melts at between 2300° and 2500°. It volatilises in the electric furnace, but less readily than the other platinum metals, so that it possesses special interest as being the least fusible and probably the least volatile metal and as the heaviest known substance, qualities which, in conjunction with its susceptibility to oxidation, and the peculiar nature of its volatile oxide, distinguish it from the other platinum metals or indeed from all other known metals.

When heated osmium combines directly with fluorine, chlorine, sulphur, and with phosphorus. It is not attacked by hydrochloric acid unless the latter contains oxygen (Matignon, Compt. rend. 1903, 137, 1051).

Although osmium, when obtained in a finely divided state by treatment of an alloy with a solvent which removes the other metal, is easily oxidised or dissolved, it is much more refractory after ignition in an inert atmosphere, and is best rendered soluble by fusion with peroxides or with a mixture of caustic alkali and nitre.

On account of its infusibility, it has been employed for the manufacture of electric-light filaments, but by reason of its high cost and the extremely small supply, its use has been abandoned in favour of tantalum filaments or of the 'osram' filaments, which are made of tungsten wire and do not contain osmium as the name might imply.

It is stated by W. C. Heraeus, that 1 part of osmium will replace 2½ parts of iridium for hardening platinum, and that the improvement in elasticity is still greater. From 1 to 20 p.c. of osmium is recommended, the alloy being made in the absence of oxidising gases, and the presence of iron and copper being carefully avoided. The alloy has been patented (Eng. Pat. 29723, 1910).

None of the osmium compounds is of technological interest, excepting the tetroxide and the osmates, as forming steps in the preparation of the metal, and (as regards the former) on account of a limited use in microscopy for staining pathological specimens. Colloidal osmium has been obtained by the reduction of its salts with hydrazine hydrate (Castoro, Zeitsch. anorg. Chem. 1904, 41, 131; Gutbier and Hofmeier, J. pr. Chem. 1905, [ii.] 71, 452).

Compounds of Osmium.

Oxides. **Osmium monoxide** OsO is a greyish-black powder formed when the corresponding sulphite is ignited with sodium carbonate in a current of carbon dioxide.

Osmium sesquioxide Os_2O_3 is obtained similarly as a black powder, or in copper-red scales by the reduction of the tetroxide. A corresponding brownish-red hydroxide is precipitated by the addition of alkalis to alkali osmochlorides.

Osmium dioxide OsO_2 is obtained similarly, and like the foregoing oxides, is feebly basic. It is bluish-black, but when prepared by heating its hydroxide in a current of carbon dioxide, it forms masses having a copper lustre. In absence of air it is very stable, but when mixed with combustible bodies it deflagrates on heating. Dried hydrated osmium dioxide has the composition $OsO_2,2H_2O$, and is gradually oxidised in air to the tetroxide (Ruff and Bornemann, Zeitsch. anorg. Chem. 1910, 65, 429).

Osmium tetroxide OsO_4, sometimes erroneously termed *osmic acid*, is prepared by heating finely-divided osmium in air or steam, or by dissolving it or the lower oxides in *aqua regia*. It may also be formed by fusing the metal with potassium hydroxide and nitrate: the mass is dissolved in water, precipitated with alcohol, and oxidised with chromic acid in a current of oxygen. The pure tetroxide so formed, when treated with potassium hydroxide, forms *potassium osmate* $K_2OsO_4,2H_2O$ (Ruff and Bornemann, *l.c.*). Osmium tetroxide forms glistening needles, which sublime readily, and give a colourless solution in water, possessing a caustic taste, and turned yellow by sulphur dioxide, then brown, green, and finally indigo-blue. When fused it boils at 100°, emitting a vapour of a powerful penetrating smell which attacks the lungs and eyes, and produces inflammation of the mucous membrane. The tetroxide also acts violently on the skin, causing painful wounds (Deville and Debray, Ann. Chim. Phys. 1859, [iii.] 56, 400; Compt. rend. 1874, 78, 1509). It is readily reduced to the lower oxides.

Osmium trioxide OsO_3 is unknown, but the corresponding *osmic acid* H_2OsO_4 is formed, according to Moraht and Wischin (Zeitsch. anorg. Chem. 1893, 3, 153), by treating the potassium salt with nitric acid. Ruff and Bornemann (*l.c.*) state, however, that they could not obtain it. A number of its salts, the *osmates*, are known.

Halides. **Osmium dichloride** $OsCl_2$, a dark brown insoluble powder, may be formed by heating the trichloride at 500° under pressure, and cooling the vapour at −50°; or in small quantity by heating the metal in chlorine.

Osmium trichloride $OsCl_3$ is formed when ammonium osmichloride is heated at 350° in chlorine (Ruff and Bornemann; *see* also Moraht and Wischin, *l.c.*). It is readily soluble in water and gives rise to the double salts known as the *osmochlorides* or *chlorosmites* M_3OsCl_6.

Osmium tetrachloride $OsCl_4$ is prepared by heating osmium in a slow current of chlorine at 650°–700°, the issuing vapours being cooled in a tube wrapped in asbestos. It forms black metallic crusts, volatilises in a vacuum to a yellow vapour, and is slowly decomposed by water with formation of the dioxide and hydrochloric acid. It gives the series of salts known as the *osmichlorides* or *chlorosmates* M_2OsCl_6 (Gutbier and Maisch, Ber. 1909, 42, 4239). For certain derivatives of these and other similar compounds, *see* Rosenheim and Sasserath, Zeitsch. anorg. Chem. 1899, 21, 122; Wintrebert, Ann. Chim. Phys. 1903, [vii.] 28, 15.

Osmium bromides and iodides are also known.

Iodo-osmous acid $I_2Os \cdot 2HI$ is formed when nascent hydrogen iodide reacts with an osmium compound. Its solution possesses a fine emerald-green colour, which rapidly turns red on exposure to air, but its salts are more stable and form permanent green solutions. This reaction may be employed as a test for osmium compounds and also for iodides in the presence of chlorides and bromides (Alvarez, Compt. rend. 1905, 140, 1254; Orloff, Chem. Zeit. 1907, 31, 1063).

Osmium tetrasulphide OsS_4 is an insoluble brown substance formed by passing sulphuretted hydrogen into a solution of the oxide.

Osmium sulphite $OsSO_3$ and numerous complex sulphites have been prepared (Rosenheim and Sasserath, *l.c.*; Rosenheim, *ibid.* 1900, 24, 420). Osmium forms complex derivatives with ammonia and also an acid $OsNO_3H$, termed *osmiamic acid*, a number of the salts of which have been prepared (Werner and Dinklage, Ber. 1901, 34, 2698; *ibid.* 1906, 39, 499). By the action of acids on the osmiamates, *nitrilo* compounds of osmium are formed (Brizard, Ann. Chim. Phys. 1900, [vii.] 21, 311; Werner and Dinklage, *l.c.*).

Osmium nitrite $Os(NO_2)_3$ and complex nitrites and *nitroso* derivatives are also known (Wintrebert, *l.c.*; and Compt. rend. 1905, 140, 585). Osmium also forms a series of *osmocyanides* very similar to the ferrocyanides. *Osmium oxalates* have been prepared by Wintrebert (*ibid.* 1900, 131, 264). Z. K.

OSMOSIS *v.* SOLUTION.

OSONES *v.* CARBOHYDRATES.

OSTEOLITE, *Calcium orthophosphate,* $Ca_3(PO_4)_2$ *v.* CALCIUM.

OTTO OF ROSES *v.* OILS, ESSENTIAL.

OUABAÏO. The poison of the Somalis. Along the whole of the west coast of Africa, especially in the country of the Somalis, occurs a tree used by the natives for the preparation of their arrow-poison, and called by them Ouabaïo. Its wood is yellowish-white, very hard and dense, odourless, but possessing a strong bitter taste. Arnaud has isolated from it (J. Soc. Chem. Ind. 1889, 211; 1888, 586) *ouabaïn*, $C_{30}H_{46}O_{12}$, which has a physiological action similar to that of strophanthin, but which is twice as toxic, the poisonous dose being about 0·2 mgrm. per kilo. of body-weight (*ibid.* 1888, 765)—Cathelineau, J. Pharm. Chem. 1889, 436; J. Soc. Chem. Ind. 1890, 101. Ouabaïn is also obtained from *Strophanthus glaber*, by extracting the seeds, from which the oil has been removed by pressure between filter paper, by shaking with alcohol for several days at a temperature not exceeding 60°. The extract is distilled and the syrupy residue is taken up with water at 50°, filtered, evaporated in a dry vacuum and recrystallised from water (Arnaud, Compt. rend. 1888, 107, 1162).

The crystals obtained by extracting *Strophanthus gratus* (Baill.), with 96 p.c. alcohol also seem identical with ouabaïn (Thoms, Chem. Zentr. 1904, i. 1277).

Ouabaïn forms pearly glistening plates, m.p. 185°–188°, and yields a crystalline hydrate with 9 molecules of water at ordinary temperature, with 4 molecules at 30° and with 3 molecules at 60°.

The rotatory power of a 1 p.c. aqueous solution of ouabaïn is $[\alpha]_D - 30 \cdot 6°$. Ouabaïn is very sparingly soluble in ether, absolute alcohol, and in chloroform; 100 c.c. of water dissolves 1·57 grams ouabaïn at 30°; 0·93 grams at 14·5° and 0·66 grams at 8°.

It is readily hydrolysed by dilute acids thus:

$$C_{30}H_{46}O_{12}+H_2O=C_6H_{12}O_5+C_{24}H_{36}O_8,$$

forming rhamnose and a red resin which is probably formed by the polymerisation of the second product of hydrolysis (Arnaud, Compt. rend. 1898, 126, 346, 1208). When dried, the resin loses $4H_2O$ and forms $C_{24}H_{28}O_4$. Alkalis do not attack ouabaïn in the cold, but by forming soluble salts they increase its solubility in water and its rotatory power: fused with potash or soda, ouabaïn decomposes at 220°–240° forming oxalic acid, a resin and carbon dioxide (Arnaud, *l.c.* 1280).

With bromine, ouabaïn gives an amorphous derivative containing 60 p.c. of halogen.

Heated with an excess of acetic anhydride at 30°–70°, ouabaïn forms the *heptacetin*, $C_{30}H_{39}O_{12}(C_2H_3O)_7$, m.p. 270°–275° (Arnaud, *l.c.* 349), whilst when ouabaïn is heated with acetic anhydride and zinc chloride at 70° and the cooled product poured into 5–6 times its bulk of water, it forms an *anhydro-hepacetin*, $C_{30}H_{37}O_{11}(C_2H_3O)_7$, m.p. 310° (decomp.), $[\alpha]_D - 68 \cdot 50$ at 85° (in alcoholic solution). On saponification, this acetin yields an acid which is similar to, but not identical with, ouabaïc acid (Arnaud, *l.c.* 1654).

Concentrated nitric acid completely oxidises ouabaïn even in the cold, forming oxalic acid, carbon dioxide and insoluble amorphous nitro derivatives. With more dilute acid (sp.gr. 1·2), no oxalic acid is formed and insoluble crystalline nitro derivatives are produced.

The *di-nitro derivative*, $C_{23}H_{24}(NO_2)_2O_6$, is formed at 40°–75° and crystallises from acetone in yellowish silky needles, m.p. 300° (decomp.). It acts as a dibasic acid and yields crystalline salts. The potassium and sodium salts form orange-red aqueous solutions, the ammonium salt crystallises in golden yellow needles. The *mononitro derivative* $C_{23}H_{25}(NO_2)O_6$ is obtained at 15° or below. It forms yellow anhydrous crystals, m.p. 280° (decomp.) and also yields alkali and ammonium salts. These nitro-derivatives are regarded as derived from the compound $C_{24}H_{36}O_8$ which is produced by the hydrolysis of the ouabaïn (Arnaud, *l.c.* 1873).

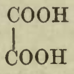
Ouabaïc acid $C_{30}H_{48}O_{13}$ is obtained by heating a dilute aqueous solution of ouabaïn in a sealed tube at 180°, or better, by heating 1 part of crystalline ouabaïn with 3 parts of strontium hydroxide in 10 parts of water for 12 hours at 100°. The hot solution is saturated with carbon dioxide, filtered, concentrated *in vacuo* and poured, little by little, into 10 times its volume of absolute alcohol. The precipitated strontium salt is dissolved in water and decomposed with sulphuric acid; it is then filtered, and the liquid evaporated *in vacuo*. It is an amorphous, yellow-white substance, m.p. 235° (decomp.), resembling gum in appearance, very soluble in water and in alcohol, but insoluble in ether. It is a dibasic acid which decomposes the alkali and alkaline earth carbonates, forming the corresponding metallic salts. The barium salt, $Ba(C_{30}H_{47}O_{13})_2$ has $[\alpha]_D^{20} - 46 \cdot 40°$ in aqueous solution (Arnaud, *l.c.* 1280).

According to Faust (Chem. Zentr. 1902, ii. 1217), *acocantherin*, isolated from *Acokanthera abyssinica* (K. Schum.), is homologous with ouabaïn, being, possibly, the dimethyl derivative. For the physiological and therapeutic action of ouabaïn *v.* Hatcher and Brody, Amer. J. Pharm. 82, 360; Müller, Zeitsch. Allgem. Österr. Apoth. Ver. 1908, 46, 319, 331.

OUTREMER. *Ultramarine* (*q.v.*); also PIGMENTS.

OVARIA SICC., OVARINUM, OVARADEN, OVADIN *v.* SYNTHETIC DRUGS.

OXALIC ACID $C_2H_2O_4$, or



$$\begin{array}{c}COOH\\ |\\ COOH\end{array}$$

This acid occurs as the acid potassium salt in wood-sorrel, garden rhubarb, and many other plants. As calcium oxalate, it occurs in many lichens and in certain urinary calculi, and in the free state is found in *Fomes* (*Polyporus*) *igniarius*, in beet leaves, and in the juice of the chick pea. It is one of the constituents of the 'organic non-sugar' in the saccharine products from beetroots, and to about 2 p.c. in 'saturation mud' of sugar refineries. It is also produced in the oxidation of carbohydrates by a large number of bacilli (Zopf, J. Soc. Chem. Ind. 1900, 386; Banning, *ibid.* 1901, 1151); and also by the action of many fungi and yeasts (Lindner, *ibid.* 1907, 628).

It is obtained as an alkaline salt when an alkaline formate is gently heated, and as the ammonium salt when an aqueous solution of cyanogen is kept for some time. The sodium salt is produced by passing carbon dioxide over sodium heated to 360°. The free acid is one of the principal products of the action of nitric acid and other oxidising agents on organic matter.

Preparation.—Moissan has synthesised potassium oxalate by the direct union of carbon dioxide and potassium hydroxide at 80°–200° in accordance with the equation—

$$2KOH+2CO_2=K_2C_2O_4+H_2$$

(Compt. rend. 140, 1209). In the laboratory, oxalic acid may be obtained by gradually adding 8 parts of nitric acid of sp.gr. 1·38 to 1 part of white sugar or starch, heating the mixture to boiling, and evaporating to about one-sixth the original bulk. The crystals obtained on cooling are recrystallised. If stronger acid be used the action is liable to become unmanageable.

This process was formerly employed on the manufacturing scale but has since been superseded by other processes; although possibly the discovery of Naumann, Moeser, and Lindenbaum (D. R. PP. 183022, 208999) that vanadium pentoxide to the extent of 0·001 to 0·002 gram per gram of sugar greatly facilitates the reaction, may give it a new lease of life. By this means, the reaction proceeds at the ordinary temperature, higher yields of oxalic acid are obtained, and no intermediate products result.

The first process to replace it was the well-known one in which sawdust is heated with caustic alkalis. Starch, straw, bran, and other vegetable matters may be similarly treated, but the best results are obtained with sawdust; fir, pine, poplar, and other soft woods, giving better results than hard woods, such as oak and beech. In order to obtain a finer product, the sawdust is sometimes treated with an alkaline lye to remove resinous and like bodies before fusion.

This process has received many modifications, the chief one being the addition of some oxidising agent. An improvement is patented by Plater-Syberg (Eng. Pat. 23682, 1893). The material rich in carbohydrates, especially wood and moss, is impregnated with caustic alkalis and then heated in presence of an oxidising agent. Hot air, or a mixture of steam and hot air, may conveniently be used as the oxidising agent. Acetates and oxalates are formed, the relative proportion of each depending on the temperature employed. By working at about 120°, acetic acid and a very small quantity of oxalic acid are formed. On raising the temperature to about 300° and increasing the quantity of hot air, the formation of acetic acid almost entirely ceases, whilst oxalic acid is formed in large quantity. Pulp suitable for paper making is obtained as a by-product.

A modification of Plater-Syberg's process is that of Zacher (Eng. Pat. 2308, 1897), in which the oxidising material is sodium peroxide or hydrogen peroxide and the heating is carried out in a vacuum. Sawdust or other cellulose material is placed in a steam-jacketed vessel which is exhausted. The contents are then slowly raised to about 70° to deprive the sawdust of moisture and air. Hot alkali lye is then admitted with continued stirring and the vacuum kept constant until a temperature not exceeding 180° is reached. Towards the end of the process, an oxidising agent such as sodium peroxide, hydrogen peroxide, or air enriched with oxygen is admitted. The finished product is dissolved in water in the same vessel, and the solution forced into an open stirring cylinder, in which it is thinned and treated with lime. The calcium oxalate obtained, practically free from carbonate, is decomposed by sulphuric acid. It is stated that a good white oxalic acid is produced by this process with one recrystallisation (*v.* also D. R. P. 103856).

Another method is to oxidise the cellulose-containing materials, in solution of caustic soda or potash of sp.gr. 1·04 to 1·1, with permanganates or manganates. The yields are better than those obtained by heating with caustic potash alone and a much lower temperature is required (Droste, D. R. P. 199583).

Oxalates are also produced together with other products by the process of Cross and Young (Eng. Pat. 28077, 1902). A nitrate or mixture of nitrates is mixed with a carbohydrate of the sugar type, an alkali or alkaline earth, and a little water, and the mass is gradually heated—ultimately to 150°–170°. The main products in this case are cyanide and oxalate. The addition of iron to the mixture produces an excess of cyanide, and the addition of sulphur, or a sulphur compound, a thiocyanate. Ammonia is evolved during the process.

A process for the preparation of oxalic acid and cellulose (Lifschütz, Eng. Pat. 1824, 1891) consists in treating wood, jute, straw, and similar materials with a mixture of dilute nitric and sulphuric acids. The brown vapours evolved, consisting of NO, NO_2 and N_2O_3, are reconverted into nitric acid. The acid liquid is used for other operations, the temperature being gradually increased as the nitric acid becomes exhausted. When this occurs the oxalic acid is crystallised out by cooling. The ligneous material after the action of the nitric acid is converted into cellulose by treatment with a weak alkaline solution.

A completely different method is that of Goldschmidt (Eng. Pat. 26172, 1897). Sodium formate is prepared by the patentee's method of heating sodium carbonate under pressure in a current of carbon monoxide (Eng. Pat. 17066, 1895). 4 parts of crystallised sodium formate are then intimately mixed with 5 parts of anhydrous sodium carbonate and rapidly heated in a molten lead bath at 400°–410°. Air is preferably excluded and the hydrogen evolved is collected. The reaction presumably follows the equation $2HCOONa=(COONa)_2+H_2$. The sodium carbonate is subsequently dissolved out with water at 33°, leaving sodium oxalate.

An improvement on Goldschmidt's method is patented by Wiens who heats formates with previously produced oxalates, in place of sodium carbonate, at 360°–410° (U. S. Pat. 714347, 1902). Koepp and Co. heat the formates with small quantities (less than 5 p.c.) of alkali hydroxide. The mixture rapidly melts, hydrogen is evolved at about 290° and the reaction is complete at 360°, occupying about half an hour in all (Fr. Pat. 331498, 1903; U. S. Pat. 748791, 1904; Eng. Pat. 9327, 1903).

Feldkamp (U.S. Pat. 802980, 1905) simplifies the sodium formate method of manufacturing oxalates by heating caustic soda in a current of carbon monoxide and dioxide (water gas or producer gas). The resulting mixture of sodium formate and carbonate is afterwards heated to a higher temperature until the evolution of hydrogen ceases, and a mixture of oxalate and carbonate is produced. The caustic alkali is then regenerated by the addition of slaked lime and precipitated calcium carbonate and oxalate decomposed by sulphuric acid (*v.* also Fr. Pat. 358785, 1905, and Eng. Pat. 22225, 1905).

The Electrochemische Werke of Bitterfeld find that oxalates are speedily and evenly produced from formates by heating in a partial vacuum to a temperature below 360°, preferably about 280°. Processes necessitating heating with sodium carbonate or oxalate are improved by working in a vacuum, but the best results are obtained by heating the formate alone (Eng. Pat. 19943, 1907; Fr. Pat. 381245, 1907; D. R. P. 204895).

Materials containing cellulose, such as peat, vinasses, sawdust, can be made to yield oxalic acid by treatment with caustic soda or potash in the presence of lime, nitrates, metallic oxides, and air between 170°–190° (Effront, Fr. Pat. 373157, 1906).

Hempel's process consists in heating caustic soda and carbonate of soda or analogous substances with carbon monoxide under pressure. At 200°–360°, formates are produced, and at higher temperatures up to 420°, oxalates. Oxalates are also produced by heating formates with or without the addition of indifferent substances at 200°–420° under pressure (Fr. Pat. 389039, 1908; Eng. Pat. 3429, 1908; 4897, 1908; 3904, 1908).

Oxalic acid is usually obtained from the oxalates resulting from these processes by dissolving them in water and precipitating as calcium oxalate, which is filtered off, washed, and decomposed with sulphuric acid. The solution is then filtered, evaporated, and allowed to crystallise. Other methods are used to some extent. McDougall and McDougall obtain oxalic acid by first preparing the potassium salt, adding a suitable sulphate (*e.g.* aluminium sulphate), and sulphuric acid, and separating the resulting alum by crystallisation, adding alcohol if necessary (Eng. Pat. 17971, 1907).

Another method is to add hydrofluoric acid, which precipitates the alum as artificial cryolite, Na_3AlF_6 (G. Müth, D. R. P. 214040). The crude acid is usually somewhat dirty from adherent mother-liquor. It is separated therefrom by a centrifugal cleanser, washed with a minimum quantity of cold water, and recrystallised.

The acid cannot be purified from oxalates by ordinary recrystallisation, but requires to be crystallised from hydrochloric acid of 10 to 15 p.c., which retains the bases as chlorides. A second crystallisation removes the acid. The pure acid may also be prepared by sublimation as described below, or by decomposing the methyl or ethyl ester with water.

For the preparation of pure oxalic acid, Schmatolla recommends crystallisation from absolute alcohol containing a drop or two of sulphuric acid, followed by crystallisation from water, the solution being allowed to stand for several hours in both cases. The crystals are then dried at 30°–40°, and finally over calcium chloride (J. Soc. Chem. Ind. 1901, 496). Riechelmann prefers to crystallise once from ether and once from water (Chem. Soc. Abstr. 1898, i. 239).

Properties.—Oxalic acid crystallises in large transparent monoclinic prisms of sp.gr. 1·641 at 4° (Joule and Playfair), containing two molecules of water.

In an atmosphere dried by sulphuric acid, it gradually loses its water. The water is also gradually evolved and the crystals become opaque when heated at 60° or 70°. As the crystals melt in their water of crystallisation at 98°, and are then somewhat difficult to desiccate, it is advisable to dry the crystals at the lower temperatures. Saturated solutions of oxalic acid lose acid even on the water-bath. The anhydrous acid (dried as above) may be volatilised at 157°, and be thus obtained in pure white needles. The temperature should not be allowed to exceed 157°, as considerable decomposition ensues and an inferior product is obtained at 160°.

When oxalic acid is dissolved in 12 parts of warm concentrated sulphuric acid, the solution gradually deposits glistening rhombic pyramids of the anhydrous acid, which rapidly absorb two molecules of water and fall to powder.

Oxalic acid dissolves readily in water and in 2½ parts of cold alcohol. It is also slightly soluble in ether, but is insoluble in chloroform, benzene, and petroleum spirit.

The following table gives the solubility of oxalic acid in water as averaged by Seidell from the results of Alluard; Miezynski (Monatsh. 1886, 7, 258); Henry (Compt. rend. 99, 1157); Lamouroux (*ibid.* 128, 998); and, at 25°, of Foote and Andrew (Amer. Chem. J. 1905, 154):—

	Grms. $(COOH)_2$ per 100 grms.			Grms. $(COOH)_2$ per 100 grms.	
t°	H_2O	Solution	t°	H_2O	Solution
0	3·45	3·33	40	21·15	17·46
10	5·55	5·26	50	31·53	23·97
20	8·78	8·07	60	45·55	31·37
25	11·36	10·21	70	63·82	38·95
30	13·77	11·91			

Oxalic acid is a powerful reducing agent. The aqueous solution is oxidised at the ordinary temperature in presence of peroxides of lead and manganese. It precipitates gold from solution of the chloride, and, in sunlight, similarly reduces platinum chloride. In presence of sulphuric acid it is oxidised by potassium permanganate with production of carbon dioxide and manganese and potassium sulphates. Oxalic acid is not acted on by sulphuric acid at the ordinary temperature, but when heated with the strong acid it is decomposed into carbon monoxide and dioxide without darkening the acid. Phosphoric acid and phosphorus penta- and trichloride also cause the evolution of these gases. Chlorine is without action on the anhydrous acid, but in presence of water it is reduced to hydrochloric acid with evolution of carbon dioxide. Hypochlorites and chlorides of easily reducible metals, such as gold and platinum, have a similar action; bromine water slowly oxidises oxalic acid to carbon dioxide and hydrobromic acid.

When exposed to bright light, oxalic acid solutions are decomposed, yielding carbon dioxide and water (Douns and Blunt. Proc. Roy. Soc. 28, 209); by oxidation with nitric acid of sp.gr. 1·4 and upwards, oxalic acid is completely decomposed into these products. According to Richardson (Chem. Soc. Trans. 1894, 452), hydrogen peroxide acts similarly (*cf.* however, Jorissen and Reichler, Chem. Zentr. 1904, i. 81); the reaction is greatly accelerated by metals (O. Sulc. *ibid.* 1899, i. 1150). Certain substances have the property of inhibiting the decomposition of oxalic acid solutions. Thymol was first recommended by Gerland (J. Soc. Chem. Ind. 1891, 25), and an examination of a number of substances has been made by Jorissen and Reichler (Chem. Zentr. 1904, i. 359). Oxalic acid is reduced by nascent hydrogen to glycollic acid.

Solutions of oxalic acid decompose carbonates, phosphates, chromates, &c., and even fluorspar. When heated with sodium or calcium chloride, the powdered acid liberates hydrochloric acid. Potassium and sodium, when heated with the dry acid, cause an evolution of hydrogen with production of a carbonate, the temperature rising to incandescence.

When heated with glycerol between 70° and 90°, oxalic acid is converted into formic acid with evolution of carbon dioxide.

The commercial acid and alkaline oxalates frequently contain organic matters which cause charring when heated alone or with sulphuric acid. Sulphates are usually present, and lead and other heavy metals frequently occur. Allen has found as much as 6·3 p.c. of lead oxide in a sample of the acid.

Oxalic acid is largely used as a ‘ discharge ’ in calico-printing and dyeing, and for bleaching flax and straw. In dyeing it is used as a substitute for cream of tartar, on account of its cheapness. In the process of ‘ chroming ’ wool, its utility lies in its power of forming double salts and in its reducing properties (Körner, J. Soc. Chem. Ind. 1895, 1044). Its property of accelerating the action of chromic acid on indigo is probably due to the formation of a chromium compound of oxalic acid with strong oxidising properties (Prud'homme, *ibid.* 1903, 359, 491; *v.* also Georgevics, *ibid.* 947). The function of oxalic acid in the indigo discharge process has also been studied by Mullerus and Margulies (*ibid.* 1893, 758); Schaposchnikoff and Michireff (*ibid.* 1902, 1276); and Jorissen and Reicher (*ibid.* 1903, 623). Werner (Chem. Soc. Trans. 1904, 1388) finds that by the action of chromic acid on oxalic acid, an acid chromic oxalate, $H_6Cr_2(C_2O_4)_6$, is produced, and his results are confirmed by Jorissen and Reicher (Chem. Zentr. 1904, i. 81). It is also employed for whitening leather, for making formic acid and its esters, and for removing ink or iron stains from fabrics, marble, &c. A solution of Prussian blue in oxalic acid is employed as a blue ink. Oxalic acid forms a constituent of several dyes. Georgevics has prepared a dyestuff which is yellow in colour, by heating resorcinol with oxalic acid at 160° (J. Soc. Chem. Ind. 1898, 837). It has great cleansing power for brass and other metal, and even for woodwork, and forms a constituent of at least one soap composition for cleaning metals, &c.

Detection and Estimation.—Solutions of calcium salts, even of the sulphate, give precipitates of calcium oxalate, on addition to solutions of oxalates, soluble in mineral acids but not in acetic acid. Free oxalic acid is precipitated by lime water and calcium acetate, but it is better to render the solution alkaline by ammonia and acidify with acetic acid before testing. Pure oxalic acid and oxalates do not char when heated alone or with concentrated sulphuric acid. It decolorises permanganate on warming. Silver nitrate produces with neutral solutions a white crystalline precipitate of silver oxalate which is very explosive when dry.

For estimating this acid, the hot dilute solution, free from mineral acids, or neutralised with ammonia and then acidified with acetic acid, is precipitated with calcium chloride or acetate, or, when sulphates are present, with calcium sulphate. For the estimation in presence of interfering substances, reference must be made to standard works on analysis. After standing for 12 hours, the precipitate is filtered off and dried, and is ignited at a dull, scarcely visible red heat to convert it into carbonate. A little saturated solution of ammonium carbonate is then added to reconvert into carbonate any of the substance which may have become causticised, and the mass is dried and heated sufficiently to remove the whole of the ammonium salt. When the precipitate does not exceed a gram, it is preferably ignited at a bright-red heat over the blow-pipe and weighed as oxide. The ignited precipitate may also be titrated with standard acid.

Another excellent method consists in dissolving the moist precipitate in dilute sulphuric acid and titrating with decinormal permanganate.

This permanganate method is applicable directly to the original substance, provided other oxidisable substances are absent.

Another alternative is to add dilute sulphuric acid to the precipitate in the crucible in sufficient quantity to convert it into calcium sulphate, and subsequently to ignite and weigh as calcium sulphate.

Hydrochloric acid is generally held to interfere with the volumetric estimation of oxalic acid, but according to Baxter and Zanetti (Amer. Chem. J. 1905, 500) oxalic acid may be estimated in the presence of hydrochloric acid with accuracy by titration with permanganate if the initial temperature of titration is not below 70° and the permanganate is run in slowly. The concentration of the hydrochloric acid should not exceed 20 c.c. dilute acid (sp.gr. 1·04) to 150 c.c. oxalic solution, containing not more than 0·3 gram crystallised oxalic acid. Gooch and Peters recommend the addition of a manganese salt (Zeitsch. anorg. Chem. 21, 185). Oxalic acid is occasionally an impurity in hydrogen peroxide in which it may be detected and estimated by nearly neutralising, adding ammonium acetate and subsequently calcium acetate, and treating the calcium oxalate by any of the well-known methods (Roche, J. Soc. Chem. Ind. 1902, 190). Oxalic acid may be estimated in acid beet leaves by the method of Schlösing (Bülow, *ibid.* 1900, 383). The methods of determination in diffusion sugar juice are reviewed by Andrelik and Stanik (*ibid.* 1900, 178).

OXALATES.

This extensive series of salts includes both normal, acid, and double oxalates, and a class of acid salts known as quadroxalates, and apparently produced by the combination of one molecule of oxalic acid with one molecule of an acid oxalate. All oxalates decompose on heating, the alkaline salts forming carbonates. Only a limited number of oxalates are of technical importance.

Potassium oxalate $C_2O_4K_2,2H_2O$ crystallises in monoclinic prisms or pyramids, readily soluble in water. The *acid salt* C_2O_4HK is found in rhubarb, sorrel, and other plants. It occurs either in anhydrous, monoclinic prisms, or in triclinic crystals containing one molecule of water. The acid salt, which is much less soluble than the normal salt, forms with oxalic acid *potassium quadroxalate* $C_2O_4KH{\cdot}C_2O_4H_2,2H_2O$, which forms triclinic crystals soluble in 20 parts of water at 20°.

Both these acid salts are sold as 'salts of sorrel' or 'salts of lemon,' and are used for removing ink stains, &c., and also for scouring metals, cleansing wood, &c., for which they are at least as suitable as the free acid.

The normal salt may be prepared by neutralising the acid with potash or potassium carbonate. The acid salt may be made by halving a solution of the acid, neutralising one part, and adding the other. The quadroxalate is similarly prepared by neutralising one-fourth of the solution and adding the remainder, or by adding 75 parts of potassium chloride to 252 parts of oxalic acid, both in saturated solution. Potassium oxalate is employed in the hot bath used in the platinotype process, and is also used in other photographic operations (*v.* PHOTOGRAPHY).

Sodium oxalate $C_2O_4Na_2$ occurs in various plants growing in salt marshes. It and the acid salt are prepared similarly to the potassium compounds. No quadroxalate has yet been prepared. The normal salt requires about 36 parts of cold water for solution. It separates from hot solutions in fine glistening needles or as a crystalline powder. The acid salt is still less soluble.

Ammonium oxalate $C_2O_4(NH_4)_2 2H_2O$ occurs in Peruvian guano. It crystallises in long rhombic prisms readily soluble in water. The acid salt is less soluble, crystallises in rhombic prisms and gives a quadroxalate isomorphous with that of potassium. These salts are prepared similarly to the potassium salts.

Calcium oxalate C_2O_4Ca is widely distributed in the vegetable kingdom and is the least soluble of the calcium salts. It occurs in rhubarb and other plants, frequently in aggregations of needle-like crystals. In larger proportions it occurs in many lichens which grow on limestone, and in certain urinary calculi. It is precipitated as a powder containing one molecule of water, by addition of a calcium salt to an oxalate. When heated to 180° it becomes anhydrous, but it reabsorbs water when exposed to the air. The acid salt has not been prepared.

Barium and *strontium oxalates* resemble the calcium salts, but are somewhat soluble in water. The neutral *magnesium oxalate*, and double oxalates of magnesium with potassium and ammonium but not with sodium, are known. The acid magnesium oxalate has not been prepared.

Ferrous oxalate occurs in lignite combined with $1\frac{1}{2}H_2O$ as *oxalite* or *humboldtine.* It may be prepared as a heavy yellow, nearly tasteless powder, almost insoluble in cold, and sparingly soluble in hot water, by mixture of ferrous sulphate with oxalic acid or an oxalate; or in fine lemon-coloured crystals by exposure of a solution of hydrous ferric oxide in oxalic acid. It is also slowly deposited from a solution of iron in oxalic acid. The artificial variety contains $2H_2O$. An acid oxalate appears to exist.

Ferrous oxalate is employed as a developer in photography. The solution used is obtained by adding ferrous sulphate solution to excess of potassium oxalate. The ferrous oxalate exists in the resulting brown solution as a double ferrous potassium oxalate $K_2Fe(C_2O_4)_2,2H_2O$. When heated it is converted into a very finely divided oxide, admirable as a rouge for optical purposes.

Ferric oxalate. The normal salt is slowly deposited as a yellow precipitate on mixing a normal oxalate with ferric chloride, or on treating freshly precipitated ferric hydroxide with a quantity of oxalic acid insufficient to dissolve the whole. The solution in oxalic acid gradually deposits ferrous oxalate on exposure to the light. Double salts with the alkalis are obtained by solution of ferric hydroxide in acid alkaline oxalates. These are considerably used in photography in the preparation of platinum printing papers. Sodio-ferric oxalate

$$Na_3Fe(C_2O_4)_3,4\tfrac{1}{2}H_2O$$

forms large green crystals. The ferric ammonium oxalate is sometimes used instead of the double citrate for producing blue prints in photography.

Antimony oxalates. The application of antimony oxalate and the double oxalates with the alkaline metals in calico-printing has been noted under article ANTIMONY, vol. i. The normal salt $Sb_2O_3 \cdot C_4O_6 2H_2O$ is obtainable by boiling antimonious chloride or oxychloride in oxalic acid, or by mixing a saturated solution of oxalic acid with a hydrochloric acid solution of the trichloride. It crystallises out as a granular precipitate. The antimony potassium oxalate $SbK_3(C_2O_4)_3,6H_2O$ is obtained in monoclinic crystals from a solution of antimonic acid in acid potassium oxalate. It is used as a mordant in dyeing. The sodium salt $SbNa_4(C_2O_4)_4,10H_2O$ is similarly prepared.

Cerium oxalate $Ce_2(C_2O_4)_3,10H_2O$ is a white, slightly granular, insoluble powder, permanent in the air, odourless and tasteless. It may be prepared by the action of oxalic acid solution on cerous oxide, or by addition of oxalic acid to a soluble cerium salt. Cerium oxalate has medicinal properties resembling those of bismuth subnitrate, and is used to prevent the vomiting of pregnancy and in certain diseases (Jolin, Bull. Soc. chim. [ii.] 21, 540).

Methyl oxalate $C_2O_4(CH_3)_2$ is obtained in rhombic tables melting at 54° and boiling at 163° by dissolving anhydrous oxalic acid in methyl alcohol and washing the crystals with cold water. Methyl oxalate is converted into oxalic acid and methyl alcohol by boiling with water. Pure oxalic acid may thus be prepared (*v.* METHYL).

Ethyl oxalate $C_2O_4(C_2H_5)_2$ is a liquid which may be obtained by slowly heating a mixture of 3 parts of the anhydrous acid and 2 parts of absolute alcohol to 100°, afterwards heating to 125° or 130° while the vapour of 2 parts of absolute alcohol is passed in. The ethyl oxalate is separated by fractional distillation. This compound is an aromatic oily liquid boiling at 186° and decomposed by water in the same manner as methyl oxalate.

A great number of aromatic esters of oxalic acid have been prepared and characterised by Bischoff and Hedenström (Ber. 1902, 3437); and also by Anselmino (Ber. Deutsch. Pharm. Ges. 1903, 494).

The decomposition of oxalates on heating, though taking place approximately according to the equation $CaC_2O_4 = CaCO_3 + CO$ in the case of calcium oxalate is in reality more complex. Some carbon is always produced during the ignition of calcium oxalate. Sodium and barium oxalates follow the courses $7Na_2C_2O_4 = 7Na_2CO_3 + 3CO + 2CO_2 + 2C$ and $8BaC_2O_4 = 8BaCO_3 + 6CO + CO_2 + C$. Magnesium oxalate gives equal volumes of CO and CO_2 and no carbon, $MgC_2O_4 = MgO + CO + CO_2$; but most other oxalates give notable quantities of carbon dioxide and carbon (Scott, Chem. Soc. Proc. 1904, 156).

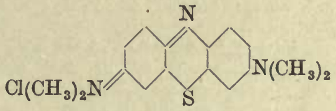
The electrolytic reduction of oxalic acid and oxalates in sulphuric acid solution to derivatives of glyoxylic acid was first patented by Portheim (U.S. Pat. 798920, 1905).

Kinzlberger and Co. (D. R. P. 163842) reduce oxalic acid, its esters, and amide electrolytically in a cell with a lead cathode and a diaphragm in presence of sulphuric acid of strengths varying from 2 to 90 p.c. monohydrate. The current density is 2 to 10 amps. per sq. cm. and the temperature must be kept low. Oxanilic acid or its derivatives in the same conditions yield phenylglycine or a derivative (*v.* also U.S. Pat. 837083; D. R. PP. 204787, 194038). Kinzlberger & Co. have since secured an additional patent for the use of electrodes of metals not attacked by sulphuric acid, particularly mercury (D. R. P. 210693). Bayer & Co. make use of sodium amalgam in the reduction of oxalic acid derivatives (D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176).

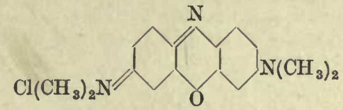
OXALIC ACID FERMENTATION *v.* FERMENTATION.

OXAMINE BLUE, -MAROON, -RED, -VIOLET *v.* AZO- COLOURING MATTERS.

OXAZINE COLOURING MATTERS.—The colouring matters of this series are closely related in structure to those of the thiazine group, the only difference in their general formulæ being caused by the replacement of the coupling sulphur atom by oxygen. Two typical examples in Capri blue and methylene blue will illustrate this statement

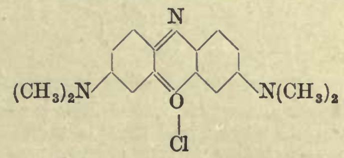


Methylene blue (thiazine)



Capri blue (oxazine)

Constitution.—The formula for Capri blue given above represents this substance as a derivative of *p*-quinone-diimide in which salt formation is produced on the imido nitrogen as in, for example, magenta. Within recent years, attempts have been made to assign to the oxazines an ortho-quinone formula of the same character as that which is now generally accepted as best expressing the structure of the colouring matters of the azine series. On this basis the formula of Capri blue becomes



in which salt formation is represented as having taken place through the passage of diad into tetrad oxygen. The work of Kehrmann and others shows that many of the properties of these compounds can be better explained by the oxonium formula than by the para-quinone structure. In the present article the oxonium formulæ have been used mainly for the sake of uniformity, although it must be remembered that it is by no means certain that the para-quinone structure of the salt is incorrect.

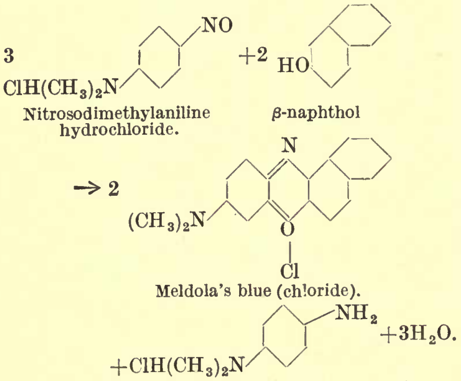
General description and methods of preparation.—The colouring matters of the series may be conveniently classed under two heads: (*a*) the basic colours; (*b*) the mordant colours.

(*a*) *The basic colours.*—These compounds are the hydrochlorides, sulphates, and, in some cases, the zinc chloride double salts of the oxazines bases. The most typical member is **Meldola's blue**, which was prepared by Meldola in 1879 and was the first colour of the series to be isolated. In the first instance the preparation was effected by allowing β-naphthol to react with nitrosodimethylaniline hydrochloride in glacial acetic acid solution. At the present time alcohol is used as a solvent and the colour is obtained by the following means.

Preparation.—A mixture containing 21 grams of β-naphthol and 53 grams of nitrosodimethylaniline hydrochloride is dissolved in alcohol and boiled for one day in a flask fitted with a reflux condenser. The colouring matter is formed in solution and is isolated as the zinc chloride double salt by adding a solution of zinc chloride until no further precipitate is obtained. The yield is 30 grams.

Properties.—The colour is a dark violet powder, soluble in water forming a bluish-violet solution. It dyes cotton mordanted with tannic acid and tartar emetic an indigo shade of blue.

Mechanism of formation.—There is no doubt that the formation of an oxazine colouring matter, in the manner described above, involves the reduction of one-third of the nitrosodimethylaniline used to *asym*-dimethyl-*p*-phenylenediamine and that the equation representing the formation of Meldola's blue can be written as follows :—



Nitrosodimethylaniline hydrochloride.

β-naphthol

Meldola's blue (chloride).

Asym-dimethyl-*p*-phenylenediamine.

It is advisable, however, to use a larger quantity of nitrosodimethylaniline than is indicated in the above equation and to employ two molecules of the aniline derivative to one of the naphthol in all reactions of this type.

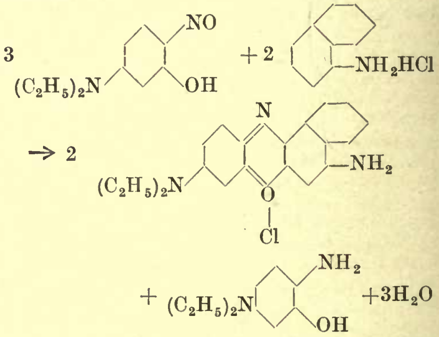
Literature.—Meldola (Ber. 1879, 12, 2065; Chem. Soc. Trans. 1881, 39, 37); Nietzki and Otto (Ber. 1888, 21, 1745); Witt (*ibid.* 1890, 23, 2247); Nietzki and Bossi (*ibid.* 1892, 25, 2994). Meldola's blue appears in commerce under other names of which the following are the more important: new blue, naphthylene blue, fast blue, cotton blue, fast navy blue and naphthol blue.

It is evident from the above equation that the formation of an oxazine colouring matter of the type of Meldola's blue might be expected to ensue when any derivative of β-naphthol is treated with a derivative of nitrosodimethylaniline provided that in the one case the adjacent position to the hydroxyl group is unoccupied and in the other the ortho- position to the nitroso group is free. In practice, however, the formation of colours of this character is confined to the simpler reaction. Nevertheless, a new method for the preparation of these colours was introduced by Reissig in 1888, and by its means a number of important colours were added to the group. The new process can be best illustrated by referring to the production of **Nile blue A**, which is produced by the interaction of nitrosodiethyl-*m*-aminophenol hydrochloride and α-naphthylamine.

Preparation.—A quarter litre flask, fitted with an air condenser, containing 10 grams of α-naphthylamine hydrochloride dissolved in 100 grams of glacial acetic acid containing 20 p.c. of water, is heated on the sand bath until the contents are at the boiling-point when 19 grams of nitrosodiethyl-*m*-aminophenol hydrochloride are added in small portions at a time. The vigorous reaction which is caused by each addition is allowed to subside before a fresh portion is added. When all the phenol has been used the mixture is allowed to boil for half an hour when the colouring matter separates as glistening crystals on cooling.

Properties.—Crystalline powder, with marked bronze reflex, soluble in water, alcohol or pyridine forming a blue solution. Dissolves in concentrated sulphuric acid forming an orange-red solution which, on dilution, passes through green to blue. It is employed for the dyeing of tannined cotton on which it produces a bright shade of blue.

Mechanism of formation.—The production of Nile blue A may be expressed by an equation similar to that given in the case of Meldola's blue, as shown below :

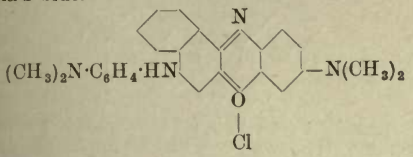


Literature.—Reissig (B. A. S. F.), E. P. 4476, 88; 11046, 91; Am. P. 431541, 90; D. R. P. 45268, 88; 74391, 91; F. P. 189359, 88; Bayer, D. R. P. 49844, 89; F. P. 198589; Möhlau and Ullmann (Annalen, 289, 111); Thorpe (Chem. Soc. Trans. 1907, 91, 324). The commercial product is usually the sulphate.

Other members of class (*a*) may be summarised as under; they are employed as tannin cotton colours.

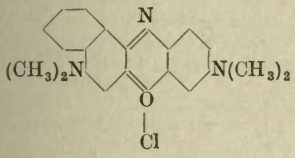
Capri blue is formed from nitrosodimethylaniline and diethyl-*m*-aminocresol (Bender, 1890), and the **Cresyl blues** (Bender, 1892) are derived from nitrosodialkyl-*m*-amino-*p*-cresol and meta- or para-diamines.

New blue R is formed by the condensation of *asym*-dimethyl-*p*-phenylenediamine with Meldola's blue.



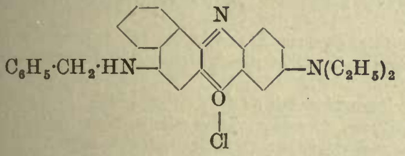
It has been already stated that this base is a by-product in the formation of Meldola's blue. It therefore follows that New blue is always present in small quantities in commercial Meldola's blue.

New methylene blue is formed by the action of dimethylamine on Meldola's blue.

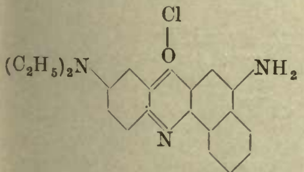


It dyes cotton mordanted with tannin a greenish-blue, fast to light and washing and is also employed for the dyeing of silk.

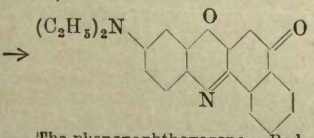
Nile blue 2B is formed by the condensation of nitrosodiethyl-*m*-aminophenol hydrochloride and benzyl-α-naphthylamine (P. Julius, 1891)



The basic colours of this series have been used for some considerable time as stains for the purpose of colouring microscope sections; like other basic colours, they stain the nitrogenous parts of the section leaving the neutral regions uncoloured. It has been shown by Lorrain Smith (J. Path. Bact. 1907, 12, 1) that certain colours of the oxazine series possess the curious property of staining sections containing nitrogenous matter and neutral fat differentially; that is to say, whilst the nitrogenous matter is coloured blue in the usual manner the neutral fat is stained red. The colouring matter which exhibits this property to the greatest degree is Nile blue A, and there is no doubt that the cause of this behaviour is due to the partial hydrolysis of the dye in solution, thus—



Nile blue A (chloride).—Blue.



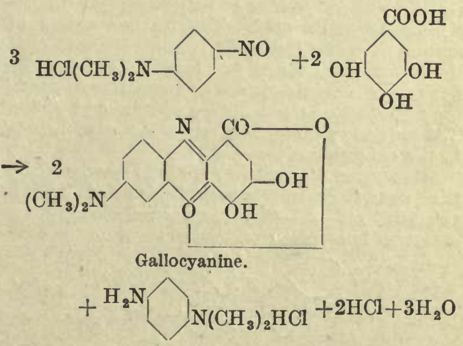
The phenonaphthoxazone.—Red.

It is found (Chem. Soc. Trans. 1907, 91, 324) that small quantities of the oxazine are formed so soon as the dye is dissolved in water and that it is readily extracted by neutral solvents. It is evident, therefore, that the staining of the neutral fat is due to the extraction of the oxazine by the fat.

(*b*) *The mordant colours.*—The colouring matters of this section are prepared by the condensation of nitrosodialkylanilines with compounds of the type of gallic acid. The oxazine contains, therefore, two hydroxyl groups in the ortho- position to the coupling oxygen atom; consequently, like alizarin, they yield insoluble lakes with metallic salts and can be employed as mordant colours. A typical member of this group is **Gallocyanine**, which can be prepared by the condensation of nitrosodimethylaniline with gallic acid.

Preparation.—A mixture of 10 grams of gallic acid and 17 grams of nitrosodimethylaniline hydrochloride is dissolved in 200 c.c. of alcohol (95 p.c.) contained in a 500 c.c. round-flask which is fitted with a reflux condenser. The reaction is completed by heating on the water-bath until a drop, removed by the aid of a glass rod, shows a deep violet spot, without a yellow rim, when placed on filter paper. The alcohol is then distilled off on the water-bath, and the dried residue, after being boiled with 200 c.c. of water and separated by filtration, is dried on porous porcelain. The colouring matter is a bronze powder insoluble in water. It dyes chrome-mordanted wool bluish-violet, and is also used for printing upon chrome-mordanted wool and cotton.

Mechanism of formation.—The course of the reaction, which is of the same character as that already shown, can be illustrated by the following equation—



Gallocyanine.

Literature.—H. Köchlin, D. R. P. 19580, 1881; E. P. 4899, 1881; Am. P. 253721, 257498; Mon. Scien. 1883 (3) 13, 292; Nietzki and Otto (Ber. 1888, 21, 1736; 1892, 25, 2994).

The other dyestuffs of this group are, for the most part, derived either directly from gallocyanine by the action of various reagents, or by processes in which gallic acid or a derivative of this substance is employed. The following are the more important members.

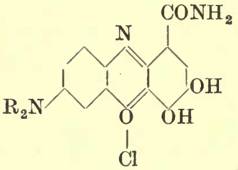
Delphine blue (Hagenbuch, 1889) is prepared by sulphonating the product formed by the action of gallocyanine hydrochloride on aniline. The **Chromocyanines** (de la Harpe and Vaucher,

1898) are formed by the action of sulphites on gallocyanines.

Indalizarin (de la Harpe and Vaucher, 1900) is obtained from the gallocyanine sulphonic acids by the action of sulphites.

Gallamine blue (Geigy, 1889) is formed by the action of nitrosodimethylaniline on gallamide.

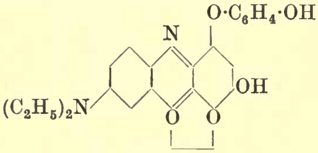
Coreine 2R (Bierer, 1893) is the corresponding diethyl derivative. It is probable that the formulæ of these compounds is best expressed by the structure—



Coreine AR is derived from Coreine 2R by the action of aniline.

The **Phenocyanines** (de la Harpe, 1893) are obtained by the action of resorcinol on the gallocyanine which is formed by the condensation of nitrosodiethylaniline and gallic acid.

Phenocyanine VS is the initial product, and **Phenocyanine TC** is formed from this by the oxidising action of air; its structure is probably represented by the formula

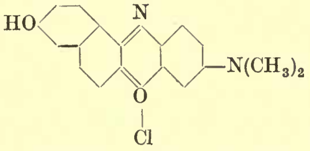


Phenocyanine TV is the sulphonic acid of Phenocyanine TC.

Gallanilic violets (Möhler, 1889) are formed by the action of nitrosodialkylanilines on the anilide of gallic acid. The further action of aniline produces **Gallanilic blue.**

The above colours are largely used for the dyeing of chrome-mordanted wool on which they produce various shades of blue and violet. The colouring matters given below also belong to the oxazine series:—

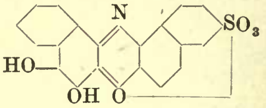
Muscarine (Annaheim, 1885) is prepared by the action of nitrosodimethylaniline hydrochloride on 2-7-dihydroxynaphthalene. Its structure is represented by the formula



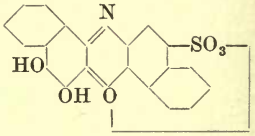
It is employed in the dyeing of tannined cotton on which it produces a fairly fast shade of blue.

Fast Green M (Bierer, 1894) is derived from muscarine by the action of aniline. Printed on cotton in conjunction with tannin, this colour produces a fine fast shade of green.

The **Alizarin Greens** (Elsässer, 1895) are prepared from β-naphthoquinone sulphonic acid and certain aminonaphtholsulphonic acids. Thus **Alizarin Green G** is produced when β-naphthoquinone sulphonic acid is condensed with 1-amino-2-naphthol-6-sulphonic acid and is represented by the formula

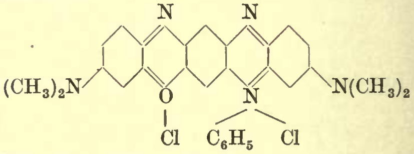


Alizarin Green B is formed from the corresponding 2-amino-1-naphthol-4-sulphonic acid and has the structure



Both colouring matters produce fast shades of green on chrome-mordanted fabrics.

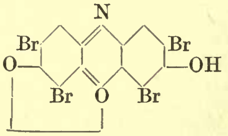
Fast Black (Bender, 1889) is formed by the condensation of nitrosodimethylaniline with *m*-hydroxydiphenylamine. The structure of this compound is, in all probability, represented by the formula



The dye-stuff produces an extremely fast shade of blue-black on tannin-mordanted cotton.

Resorcin Blue (Ullrich, 1898) is always produced directly on the cotton fibre by treating the material, impregnated with tannic acid and resorcin, with nitrosodimethylaniline.

Fluorescent Blue (Iris Blue) (Weselsky and Benedict, 1880) is made by the bromination of resorufin, a compound which is produced by heating nitrosoresorcinol with resorcinol in the presence of concentrated sulphuric acid. It has the structure



and dyes silk and wool a fairly bright shade of blue, the dyed fabric retaining, to a certain extent, the brownish fluorescence of the dye solution. J. F. T.

OX-GALL *v.* Bile.

OXIDISED OILS *v.* Oils, Fixed, and Fats.

OXINDOLE *v.* Amino acids (aromatic).

OXONITE *v.* Explosives.

OXOZONE *v.* Ozone.

OXYACANTHINE $C_{18}H_{19}NO_3$. An alkaloid associated with berberine and berbamine in berberis root (Hesse, Ber. 19, 3190).

OXYANTHRARUFIN. *Oxychrysazin v.* Alizarin and allied colouring matters.

OXYAZO- DYES *v.* Azo- dyes.

OXYCAMPHOR *v.* Synthetic drugs.

OXYCANNOBIN *v.* Resins.

OXYDASES. The term 'oxydase' was first applied by Bertrand to the group of oxidising ferments which possess certain characteristics common to enzymes. Although there is much in the behaviour of the oxydases which distinguishes them sharply from other enzymes, particularly the fact that they are generally associated with manganese, it is customary to regard them as enzymes and to define them as substances which, under physiological conditions, rapidly carry oxygen to materials on which otherwise oxygen would act very slowly.

Oxydases act as catalysts, their activity rises to an optimum with increase of temperature and then falls with a further rise: it is destroyed on boiling. They are insoluble in alcohol, absorbed by colloidal precipitates and unable to dialyse. Finally, they are selective in their action, different oxydases acting only on certain groups of more or less closely related materials.

The power of effecting oxidation is accompanied by a marked absorption of oxygen from the surrounding atmosphere.

Oxydases are so universally distributed and take part in so many natural phenomena, particularly those which are manifested externally by colour changes, that it is surprising so little is understood as yet about the mechanism of their action. A number of reagents have been employed in their study: few of these are really satisfactory.

The most extensively used are guaiacum, which gives a blue colouration and precipitate; quinol, which is oxidised to quinone (Bertrand, Compt. rend. 1894, 18, 1215); pyrogallol, which gives insoluble purpurogallin (Bach and Chodat, Ber. 1904, 37, 1342); vanillin, which forms insoluble dehydrovanillin (Herzog and Meier, Zeitsch. physiol. Chem. 1908, 57, 35; 1909, 59, 57). The behaviour of tyrosinase is studied on tyrosine which becomes first red, then black and finally gives a black precipitate. Salicylic aldehyde, benzidine, the leucobase of malachite green, phenolphthalein, &c., have also found employment. [For a complete list of oxydase reagents and references to the original papers, *v.* Kastle, U. S. Treasury Dept. Hygienic Laboratory, Bulletin No. 59.]

The better known oxydases are:—

1. *Laccase*, which oxidises guaiacum, quinol, tannin, &c., and is very widely distributed in plants.

2. *Tyrosinase*, which oxidises tyrosin and allied substances: it occurs in both plants and animals. Less studied have been—

3. *Aldehydase*, an animal oxydase, which oxidises salicylaldehyde and other aromatic aldehydes.

4. *Indophenol oxydase*, which is widely distributed in animal tissues: it forms indophenol from α-naphthol and *p*-phenylenediamine (Röhmann and Spitzer, Ber. 1895, 28, 567). In addition, enzymes known as *peroxydases*, which oxidise reagents only in presence of a peroxide like hydrogen peroxide, are universally distributed in living cells and tissues.

The view is gaining ground that oxydases are not entities but in reality mixtures of a peroxydase and an unstable organic peroxide (Moore and Whitley, Biochem. J. 1909, 4, 136; Bach and Chodat, Ber. 1903, 36, 606). Many plants contain organic bodies capable of autoxidation, thereby becoming organic peroxides. This superoxidation may be caused by an enzyme—the *oxygenase*. These two components, peroxide and peroxydase, are essential to the constitution of an oxydase.

Catalases are ferments which decompose hydrogen peroxide but cannot effect the oxidation of oxydase reagents, a distinction first drawn by Loew (Bulletin No. 66, U. S. Dept. Agric. 1901). They are very widely distributed in vegetable and animal tissues. Catalase is soluble in water and destroyed by heat. Considerable interest attaches to the catalase (hemase) of blood (Senter, Zeitsch. physikal. Chem. 1903, 44, 257; 1905, 51, 673).

It has been suggested that the function of catalase is to protect the organism against excessive oxidation, but the inability to decompose substituted organic peroxides or oxygenases (Bach and Chodat, Ber. 1903, 36, 1756) and other facts are against this view and the question is as yet but imperfectly understood.

Peroxydases and catalases are so widely distributed in living tissues that their presence might almost be used as a chemical test for vital activity. They are characterised by great stability: thus the peroxydase of horse-radish is not entirely destroyed when its solution is boiled for a short time. The activity of a weak oxydase is greatly increased by a peroxydase, more especially by that from the same source as itself. They gradually lose their activity during the oxidations which they bring about.

Peroxydases appear invariably to contain manganese, and Bertrand (Compt. rend. 1897, 124, 1032, 1355) has shown that the oxidising power of laccase is proportional to the amount of manganese present; further, that the addition of a small amount of manganese greatly increased the oxidising power of lucerne laccase. He therefore regards manganese as the co-ferment of laccase in the same way as hydrochloric acid is the co-ferment of pepsin. The manganese cannot be replaced by other metals in the case of laccase, but iron and other metals have similar functions with other enzymes. Colloidal suspensions and solutions of these metals have been shown to form artificial peroxydase systems. The subject is a complex one. For literature, *see* Kastle, *l.c.*

Tyrosinase. An oxidising ferment acting on tyrosine is widely distributed in both plants and animals. When the enzyme is added to a solution of tyrosine, the mixture becomes red, then black and deposits finally a black precipitate. The amount of action is conveniently measured by titrating with 0·002 normal potassium permanganate after the addition of sulphuric acid (Bach, Ber. 1908, 41, 216) until the colour of the titer disappears.

This change is responsible for the reddening and subsequent blackening observed in certain fungi and in the roots and tubers of plants. Tyrosinase is also of importance in the formation of animal pigments—melanins as they are termed (*v.* von Fürth and Schneider, Beitr. chem. Physiol. Path. 1901, 1, 229; also von Fürth and Jerusalem, *ibid.* 1907, 10, 131).

Tyrosinase is entirely different from laccase which usually accompanies it in plants. The peroxydase of laccase activates hydrogen peroxide towards guaiacum, quinol, pyrogallol, &c., but not towards tyrosine, whilst the peroxydase of tyrosinase acts only on tyrosine and certain amino compounds and does not affect the laccase reagents.

Vegetable tyrosinase is best obtained from fungi—species of *Russula* or *Agaricus*—or from wheat bran (Bertrand and Mutermilch, Compt. rend. 1907, 144, 1385). The young fresh fungus is macerated with chloroform water or with glycerol, or the enzyme may be precipitated from the aqueous extract by alcohol (Bach, Ber. 1908, 41, 221). 300 c.c. of clear expressed fungus juice is poured into 1·5 litres of 96 p.c. alcohol: the precipitate is filtered, washed with alcohol and dried in a vacuum. The activity depends on the age of the fungus.

To obtain it from wheat bran, 1 part is allowed to stand with 4 parts water—the mixture is centrifuged and the solution mixed with 3 vols of 95 p.c. alcohol. The precipitate is separated, washed, and dissolved in distilled water. The enzyme is again precipitated by alcohol, collected and dried *in vacuo*: the substance obtained amounts to 0·8 p.c. and contains no laccase.

Sources of animal tyrosinase are the ink sac of the cuttle fish and the pupae of the butterfly of the species *Deiciphilia euphorbiæ* (von Fürth and Jerusalem, *l.c.*).

Tyrosinase is sensitive to the action of acids and alkalis and certain poisons, particularly hydrocyanic acid. It obeys the laws of mass action in the production of melanin from tyrosine (Bach, Ber. 1908, 41, 221).

Tyrosinase acts equally well on racemic, dextro- and lævo- tyrosine. It gives characteristic colours with compounds analogous to tyrosine containing a phenolic hydroxyl (Bertrand, Bull. Soc. chim. 1908, [iv.] 3, 335). It gives colour changes with homogentisic acid and tryptophane and with polypeptides containing tyrosine; the latter are not coloured like tyrosine but become yellow, then orange and finally mahogany red. The nature of the amino acid modifies the colour (Abderhalden and Guggenheim, Zeitsch. physiol. Chem. 1907, 54, 331; also Chodat and Staub, Arch. Sci. Phys. Nat. 1907, 23, 265; 1907, 24, 172).

Laccase is of almost universal distribution in the vegetable kingdom but its occurrence in animals is rare. It is soluble in water and active aqueous extracts are readily obtained from most plant materials, the potato and cabbage being convenient sources. It is more stable towards heat and alcohol than tyrosinase, the latter being destroyed at 70^c: laccase is killed on boiling. Most acids and substances, such as hydrogen cyanide and hydrogen sulphide, destroy its activity.

It may be salted out from solution by ammonium sulphate. It is not specific in its action but promotes the oxidation of a large number of easily oxidisable substances. It is responsible for the colour changes occurring in cut fruits like apples, pears, &c., the brown colour formed being considered to be due to the oxidation of tannin by laccase (Lindet, Compt. rend. 1895, 120, 370; Kastle and Loevenhart, Amer. Chem. J. 1904, 31, 606).

A very complete and critical summary and bibliography of the literature bearing on oxydases is given by J. H. Kastle, Bulletin No. 59, Hygienic Laboratory, U. S. Treasury Dept. 1910. E. F. A.

OXYGEN. Sym. O. At.wt. 16.

Historical note.—The first recognition of the *rôle* of oxygen in nature would seem to date from the eighth century. The Chinese Philosopher Mao-Khóa then promulgated a theory based on his experiments, that all matter was composed of two fundamental elements, Yang (the strong or primary) and Yin (the weak or secondary). In air both these elements were present combined with elemental fire. The Yang (or more complete air) could be obtained purer by burning in air certain of the metals, sulphur or charcoal, which robbed the air of some of its Yin; whilst Yin, never occurring pure in the air, could be obtained by heating certain minerals (the identity of which is not clear) and especially Hhò-siaō (probably nitre). Mao-Khóa recognised that the Yin of the air was also present in water, though here it was so closely bound to Yang that its separation was difficult. The important part taken by Yin in combustion and respiration was recognised. Leonardo da Vinci was the first European to recognise, towards the end of the fifteenth century, the non-elemental character of the air and to state that only one part of it was concerned in combustion and respiration. Robert Hooke, in Micrographia, published in London in 1665, recognised the same fact, and that the same constituent, or at least a very similar one, was present in nitre. Mayow in 1674 recognised that the *active* constituent of air which supports combustion forms only part of the atmosphere, and that the same substance is present in nitre, and is given off when nitre is heated strongly. Mayow termed this gaseous constituent of air and nitre *spiritus vitalis, spiritus nitro-aëreus*, and *pabulum igneo-aëreum.* Borch (1678) carried the work of Mayow rather further, and Hales (1727) obtained oxygen by heating nitre, and collected the gas over water in nearly theoretical quantity, but failed to recognise its character. Priestley obtained the gas on August 1, 1774, by heating mercuric oxide in a glass vessel by the heat of the sun's rays concentrated on the oxide by means of a burning glass, and gave it the name *dephlogisticated air.* The gas was isolated independently, and almost simultaneously (probably in 1771, though the publication of this result was only made several years later), by the Swedish chemist Scheele, who applied to it the term *empyreal* or *fire-air.* Condorcet soon after suggested the name *vital air.* Lavoisier regarded it as an essential constituent of all acids, and hence gave it its present name *oxygen* (from ὀξύς, acid, and γεννάω, I form). The later discovery that hydrochloric and the other halogen acids contained no oxygen showed that this substance is not necessarily present in acids, but the name has been retained. The discovery of oxygen was the means of leading Lavoisier to the true theory of combustion (*see* Jörgensen, Die Entdeckung des Saurstoffes, Stuttgart, 1909).

Occurrence.—Oxygen is the most abundant and the most widely distributed element in nature. In the free state it occurs, mechanically mixed with nitrogen, in the atmosphere, of which it forms about 21 p.c. by volume, and more than 23 p.c. by weight. In the combined state it forms eight-ninths by weight of all the water on the globe, and nearly half of the three chief constituents of the earth's crust, viz. silicious rocks, chalk, and alumina. Most minerals—the chief exceptions being rock salt, fluorspar, blende, galena, and pyrites—contain oxygen in considerable proportions. It is an essential constituent of all animal and vegetable tissues and fluids. It is absorbed in large quantities from the atmosphere by animals and vegetables during respiration, but this abstraction is practically counterbalanced by the oxygen evolved by green foliage under the influence of sunlight.

Preparation.—A. *On the laboratory scale.* Oxygen may be obtained by the action of heat on the oxides of mercury, silver, gold, and platinum; the peroxides of hydrogen, the alkalis, barium, lead, and manganese; the chlorates, bromates, iodates, nitrates, and dichromates of potassium and other bases; it is evolved during some chemical reactions, and during the electrolysis of many substances, notably of water.

Of the modes of preparation most convenient for use in the laboratory, or of interest from historical or theoretical considerations, the following are the principal:—

1. By heating red oxide of mercury it splits up into vapour of mercury (which condenses) and oxygen: $2HgO=2Hg+O_2$. This reaction is of interest as being that by which Priestley first obtained oxygen.

2. By heating manganese dioxide to a bright-red heat it gives up one-third of its oxygen: $3MnO_2=Mn_3O_4+O_2$. The oxide is best heated in an iron bottle placed in a furnace, as glass vessels will not stand the high temperature required. 100 parts by weight of the pure peroxide yield 12·3 parts by weight of oxygen.

Manganese dioxide occurs in large quantities in nature as the mineral *pyrolusite*, and thus forms a cheap source for the preparation of quantities of a few hundred feet of oxygen, but the high temperature required makes the process somewhat inconvenient. Pyrolusite usually contains about 70 p.c. of the dioxide, and therefore gives a lower yield of oxygen than that indicated by the equation.

3. Potassium chlorate is a very convenient and economical source for small quantities of oxygen for lecture and laboratory purposes. When gradually heated in a hard glass retort or flask, this salt melts at about 360°–370°, and at about 370°–380° evolution of oxygen commences. After some time the fused mass thickens from the formation of the perchlorate, which, at a still higher temperature, is also decomposed. Ultimately, therefore, potassium chloride alone remains in the generating flask, the whole of the oxygen having been given off according to the equation: $2KClO_3=2KCl+3O_2$. 100 parts by weight of chlorate yield 39·16 parts by weight of oxygen, or 1 oz. of chlorate 1·8 gallons of the gas. The oxygen obtained is very pure.

The temperature required in this decomposition is too high for convenient use, as the glass vessels employed in the preparation of the gas often soften under the great heat, and yield to the pressure of the contained gas. When metallic vessels are used the heating must be very carefully watched, since the decomposition being exothermic (*i.e.* heat being evolved during the reaction), when once decomposition has set in, the evolution of gas is liable to become very violent. If the potassium chlorate be mixed with about one-eighth its weight of some non-fusible oxide, such as oxide of copper, oxide of iron, or manganese dioxide, the evolution of oxygen takes place at about 240°, or considerably below that at which the salt fuses, and is much more regular. The addition of a little spongy platinum answers the same purpose.

The gas prepared in this way almost invariably contains traces of chlorine, which are removed, when necessary, by passing the gas through a solution of caustic soda.

Commercial manganese dioxide (pyrolusite) is sometimes adulterated with coal-dust. If such dioxide is heated with potassium chlorate the coal-dust burns—often with explosive violence—at the expense of the oxygen of the chlorate, and this has been the cause of fatal accidents. It is, therefore, advisable to test the dioxide before use by heating a small quantity in a test tube with some chlorate.

The action of these oxides in facilitating the decomposition of the potassium chlorate is probably due to the transient formation of higher oxides of extreme instability. The oxides which show this action most markedly are those which form unstable higher oxides. The action of spongy platinum is less clear, but is probably connected with the tendency of that substance to condense oxygen on its surface.

4. By heating a concentrated solution of bleaching powder (or any hypochlorite) to which a small quantity of oxide of cobalt has been added, it is resolved into calcium chloride and oxygen: $2CaOCl_2+4CoO=2CaCl_2+2Co_2O_3$ and $2Co_2O_3=4CoO+O_2$. The decomposition is shown in two stages to exhibit the action of the oxide of cobalt. It is not necessary to use pre-formed oxide of cobalt, as any salt of cobalt will answer the same purpose. The oxides of copper, iron, and nickel are similar in their action. Instead of a solution a thick paste of bleaching-powder and water may be used if a small quantity of paraffin oil is added. The oil, floating on the surface of the pasty liquid, prevents the frothing which would otherwise take place. The best temperature for the evolution of gas is about 70°–80°, at which a steady stream may be obtained.

Another modification of this method is to pass a stream of chlorine into boiling milk of lime to which a small quantity of a salt of copper, cobalt, or nickel has been added. Oxygen gas is given off according to the equation $2Cl_2+2Ca(OH)_2=2CaCl_2+2H_2O+O_2$.

5. From various peroxides—

(*a*) When an intimate mixture of 3 mols. barium peroxide (2 parts by weight) and 1 mol. potassium dichromate (1 part by weight) is treated with dilute sulphuric acid, oxygen is abundantly evolved at ordinary temperatures (Robbins, Pharm. J. [ii.] 5, 436).

b. If 500 c.c. of commercial hydrogen peroxide (10 p.c. solution) are introduced into a suitable generating flask, and a solution of 25 grms. of potassium permanganate in 500 c.c. of water, mixed with 25 c.c. concentrated sulphuric acid, is allowed to flow gradually into the mixture from a dropping funnel, oxygen will be rapidly evolved without the application of heat, the amount of oxygen obtained from these quantities being about 10 litres.

(*c*) Baumann recommends (Zeitsch. anorg. Chem. 1890, 79) charging a Kipp apparatus with pieces of pyrolusite of 2–4 mm. diameter and using as the activating liquid commercial hydrogen peroxide to which, while well cooled, 150 c.c. of strong sulphuric acid has been added per litre. The evolution of the oxygen is steady and continuous. Neumann recommends the use of cubes made from 2 parts barium peroxide, 1 part pyrolusite, and 1 part gypsum with hydrochloric acid of sp.gr. 1·12 as activating liquid, but the oxygen evolved by this method contains traces of chlorine.

(*d*) If water is dropped on to broken pieces of fused potassium, sodium or potassium-sodium peroxide, a steady stream of oxygen is evolved. Walter recommends fusing 100 grms. sodium peroxide, 100 grms. potassium nitrate, and 25 grms. magnesia; hydrochloric acid is then dropped on to the cold broken-up mass.

(*e*) If a mixture of equal parts of sodium peroxide and a salt containing water of crystallisation, such as sodium sulphate, is gently heated, oxygen is evolved in a steady stream.

6. On passing a mixture of steam and chlorine through a red-hot porcelain tube, filled with fragments of porcelain to increase the heating surface, the chlorine combines with the hydrogen of the water and oxygen is liberated: $2H_2O+2Cl_2=4HCl+O_2$.

7. By the electrolysis of water slightly acidulated with sulphuric acid, the water is resolved into hydrogen and oxygen, the latter appearing at the positive pole: $2H_2O=2H_2+O_2$. This forms a convenient method of obtaining small quantities of pure oxygen, such as are required in gas analysis.

8. Oxygen may be prepared from such highly oxidised compounds as peroxides of lead and manganese, potassium dichromate and permanganate, &c., by the action of sulphuric acid. These are, however, seldom used as sources of gaseous oxygen, but are very useful as oxidising agents. Thus hydrochloric acid, when treated with sulphuric acid and potassium permanganate, is oxidised to hypochlorous acid, and alcohol treated with sulphuric acid and manganese dioxide yields aldehyde and water. The following equations represent the changes which take place when manganese dioxide and potassium dichromate are respectively treated with sulphuric acid:

$$2H_2SO_4+2MnO_2=2MnSO_4+2H_2O+O_2$$

and $$8H_2SO_4+2K_2Cr_2O_7=2K_2SO_4+2Cr_2(SO_4)_3+8H_2O+3O_2.$$

The change is rendered visible in the latter case by the formation of a deep-green salt of chromium, the solution being previously of a red colour.

9. When fresh leaves, such as mint or parsley, are exposed to the influence of sunlight in an inverted cylinder filled with water saturated with carbon dioxide and standing in a basin of the same liquid, oxygen appears after a time in minute bubbles on the leaves, and collects in the upper part of the jar. This method of liberating oxygen is of interest as being that which occurs in nature, by means of which the loss of atmospheric oxygen continually taking place from combustion and respiration is replaced.

Several other modes of preparation which, in addition to their theoretical interest, are of practical and technical value, will be treated of in the following section.

B. *On the industrial scale.* 1. The first method proposed for obtaining oxygen on the large scale was the ignition of nitre, and this method, in various modifications, has formed the basis of several patents. The first oxygen patent occurring in the records of our Patent Office, is No. 12536, S. White, 1849. But the oxygen so obtained was contaminated with oxides of nitrogen, and this method has not proved advantageous. It deserves mention, however, as being the means by which Priestley first obtained impure oxygen in 1771. He then believed the gas to be 'fixed air' (carbon dioxide), and only recognised his mistake 3 years afterwards, when he obtained oxygen from mercuric oxide.

2. By heating manganese dioxide. This was formerly one of the cheapest methods of preparing oxygen on the commercial scale.

3. By heating a mixture of potassium chlorate and about one-eighth of its weight of manganese dioxide. Though more costly than the last-named, this method is more easily carried out, and was, until within the last 30 years, almost exclusively employed in the preparation of the considerable quantities of oxygen used for lime-light purposes.

4. By the decomposition of sulphuric acid by heat: $2H_2SO_4=2SO_2+2H_2O+O_2$. The sulphuric acid is allowed to drop on red-hot surfaces, and is thus decomposed. If the oxygen alone is wanted, the emergent gaseous mixture is passed over media suitable for the absorption of the water and sulphur dioxide. As a method for the preparation of oxygen only this process has not found much favour, but it has been very largely and successfully used in the preparation of sulphur trioxide, where, the water being removed by a desiccating agent, a mixture of sulphur dioxide and oxygen in the desired proportions is at once obtained. It is the process suggested by Squire in his patent for the manufacture of sulphur trioxide (Eng. Pat. 3278, 1875).

5. By the dialysis of air. Many attempts have been made to utilise the laws of diffusion of gases through porous septa, discovered by Graham, or the property of caoutchouc when in thin layers to allow oxygen to pass through it more readily than nitrogen. Several patents have been taken out for processes of this kind, but with no practical success, and the phenomena do not seem likely to lend themselves to the production of oxygen on the large scale.

6. Better success has attended the endeavour to make use of the greater solubility of oxygen than of nitrogen in water or other solvents. Mallet, who took out a patent for this process (Eng. Pat. 2137, 1869), compressed the air over water. The coefficient of solubility of oxygen in water is about twice that of nitrogen. The oxygen was, therefore, dissolved in greater proportion than the nitrogen, and when the excess of pressure was removed and the dissolved gases extracted by the aid of a vacuum pump, the amount of oxygen in the gaseous mixture was greater

than in air. This mixture was then repeatedly subjected to the same treatment, when, after about eight absorptions, nearly pure oxygen was obtained. The following table, given by Mallet (Dingl. poly. J. 199, 112), shows the composition of the gaseous mixture at each successive stage of the operation:—

Atmospheric air	Composition after successive absorptions							
	1	2	3	4	5	6	7	8
N=79	66·7	52·5	37·5	25·0	15·0	9·0	5·0	2·7
O=21	33·3	47·5	62·5	75·0	85·0	91·0	95·0	97·3

This process was used by Phillips in 1871–72 to obtain oxygen for his experimental lighting of part of Cologne by special oxygen-fed oil lamps, but beyond this does not appear to have been practically applied.

7. By the alternate oxidation and de-oxidation of cuprous chloride. Cuprous chloride, if exposed to air, and especially to moist air, is oxidised to cupric oxychloride, and this, when heated to dull redness, gives off oxygen, and is reconverted into cuprous chloride.

(*a*) $2Cu_2Cl_2+O_2=2Cu_2OCl_2$,
(*b*) $2Cu_2OCl_2=2Cu_2Cl_2+O_2$.

Mallet obtained patents (Eng. Pat. 2934, 1865, and 3171, 1866) for the practical utilisation of this method as a continuous process for obtaining oxygen from the air, but it has not been found economically available on the large scale.

8. By the alternate formation and decomposition of alkaline manganates. When an oxide of manganese is mixed in suitable proportions with a caustic alkali (potash or soda), and is subjected to the action of air at a moderately high temperature, an alkaline manganate is formed. If this manganate is then heated to a bright-red heat, and a current of steam passed over it, it is resolved into its original constituents with evolution of oxygen (C. M. Tessié du Motay and C. R. Marechal, Eng. Pat. 85, 1866).

$$2MnO_2+4NaOH+O_2(air)=2Na_2MnO_4+2H_2O;$$
$$2Na_2MnO_4+2H_2O=Mn_2O_3+4NaOH+3O;$$
$$Mn_2O_3+4NaOH+3O(air)=2Na_2MnO_4+2H_2O.$$

The mixture was introduced into horizontal retorts, which were heated to a dull-red heat while a current of air was passed through. After oxidation was complete the supply of air was cut off, the retorts were heated to a bright-red heat and a current of steam admitted when oxygen was evolved. The retorts were then allowed to cool again to a dull red, the passage of air again commenced, and so on. The mixture was said to undergo no deterioration, and a continuous and very economical method of obtaining oxygen seemed attained. Works were erected, and the process carried out on the large scale at Paris, Lille, Brussels, Vienna, and New York, and large quantities of oxygen were made. A large part of Paris was laid with a double system of piping with the intention of lighting that city with the oxy-hydrogen light, and the New York Company carried out by the same light the lighting of the works during the building of the Brooklyn bridge. But it was found in practice that the mixture did deteriorate, the yield of oxygen rapidly diminishing, and finally almost ceasing. This was probably due to the difficulty of maintaining the intimate mixture of the easily-fusible, hygroscopic and very soluble soda with the manganic oxide, the former settling to the bottom through the combined effect of the heat and steam used.

Many attempts have been made to overcome the difficulties of the manganate process. Bowman (Eng. Pat. 7851, 1890) claimed to have overcome this difficulty by making the alkaline manganate in a granular form and dusting over the granules, whilst still in a plastic condition, with oxide of copper. Parkinson (Eng. Pat. 14925, 1891) claimed improved modes of preparation of the material together with the use of a vacuum in place of steam to cause the evolution of the oxygen. The manganate material, in upright iron retorts, was heated to about 1200°, and air pumped in under pressure to effect oxidation, the pumps were then automatically reversed and the oxygen drawn off under greatly reduced pressure. Fanta's claim (Eng. Pat. 3034, 1891) mainly consisted in increased stability of the material by the use of excess of caustic soda, and Webb's resembled Bowman's, except that the pieces of manganate material were dusted over with manganese peroxide instead of with oxide of copper. In Chapman's process (Eng. Pat. 11504, 1892) 'oxide of manganese (or the like) in a powdered form is kept suspended in fused soda (or the like) so that the charge is practically in the condition of a liquid,' and the alternate supplies of air and steam were driven into the liquid at the bottom, thereby keeping the oxide in a state of suspension. But though these modifications have been tried on the practical scale, none of them has proved commercially economical.

9. Kassner (Eng. Pat. 11899, 1889) found that when an intimate mixture of lead oxide and chalk is heated to 600° in contact with the air, a calcium plumbate Ca_2PbO_4 is formed. If this plumbate is then introduced into a solution of potassium or sodium carbonate it is decomposed, an insoluble precipitate of calcium carbonate and lead peroxide is formed, and caustic potash or soda remains in solution. This is removed by decantation, and the precipitate washed. The precipitate, in which the lead peroxide is, of course, the active part, may then either be used directly as an oxidant, or it may be introduced into a decomposing vessel, dried with superheated steam, and heated to about 500°, when oxygen is evolved, the mixture of lead oxide and calcium carbonate left being then ready for regeneration. The decomposition of the plumbate may also be effected by suspending it in water and treating with carbonic acid. The following equations indicate the reactions taking place:

$$2CaCO_3+PbO+O(air)=Ca_2PbO_4+2CO_2;$$
$$Ca_2PbO_4+2Na_2CO_3+2H_2O$$
$$=4NaOH+2CaCO_3+PbO_2;$$
$$2CaCO_3+PbO_2=2CaCO_3+PbO+O.$$

The inventor lays stress on the cheapness of the process owing to the caustic soda obtained being a valuable by-product. The complexity of the process and the large amount of labour entailed by it, leave very little chance of its being practically applicable, except possibly in chemical works, where it is to be used in conjunction with the manufacture of caustic alkali, and even here its economy is very doubtful.

The decomposition of the plumbate into lime and lead peroxide may also be effected *in situ* by means of a current of moist furnace gases at 80°–100°, and the oxygen then liberated by raising the temperature. The great changes of temperature, however, thus involved, render the method impracticable, and in addition the sulphur impurities in the furnace gases rapidly deteriorate the mixture.

Salamon (Eng. Pat. 6553, 1890) proposes to decompose the calcium plumbate without removing it from the producer in which it is formed by allowing the temperature to fall 'to a certain point,' and then introducing a current of pure carbon dioxide. The following reaction then occurs:

$$Ca_2PbO_4+2CO_2=2CaCO_3+PbO+O.$$

This necessitates the use of at least four times the volume of carbon dioxide as of oxygen obtained, a condition which at once puts the process out of the question as a technical and economical one. It has been suggested that the quantity of pure carbon dioxide required may be largely reduced by carrying out the earlier part of the reaction by means of the carbon dioxide in furnace gases, and using it pure only at the last. But the drawbacks so introduced fully neutralise any advantage.

10. By the alternate formation and decomposition of barium peroxide. In 1851 Boussingault found that when barium oxide (baryta) is heated to a dull-red heat in a current of air it is converted into barium peroxide, and that at a higher temperature this peroxide is again resolved into barium oxide and oxygen. But his attempts to utilise this reaction as a practical and economical source of oxygen failed owing to the fact that after a few oxidations and deoxidations the baryta lost its power of re-absorbing oxygen. Many other attempts were made to overcome this difficulty, but for long without success. In 1879, however, the MM. Brin frères were more successful, and took out a patent for the process (Eng. Pat. 1416 of 1880). Further improvements were made under the auspices of the company formed to develop and work the patents, and the process was made practical and economical, and was worked on a large scale at various places.

The permanence of the baryta is mainly dependent on its physical condition, the use of reduced pressure during deoxidation, and consequent avoidance of excessively high temperatures, and the careful purification of the air used. It was found possible to dispense with change of temperature in the reaction, change of pressure being alone trusted to for determining the respective phases of oxidation and deoxidation. Neither the oxidation nor the deoxidation is as complete as when two temperatures are used, and the yield per operation is much less. But the duration of the operation was reduced from about 4 hours to 8–15 mins., and the total daily yield therefore largely increased. At the same time the operation was much simplified, the wear and tear of furnace, retorts, &c., very greatly reduced, and the fuel required lessened. Labour was also economised, the multiplied reversals of cocks, &c., necessitated by the single-temperature method of working being effected automatically by reversing gear designed by K. S. Murray. The labour required was therefore little more than that needed for stoking the furnace, and oiling and supervising the pumps, &c. The oxygen obtained had a purity of about 93–96 p.c.

For a producer capable of delivering 10,000 cubic feet of oxygen per 24 hours the consumption of coke in the furnace is about 12–15 cwt. per day, and for plant of that or smaller size the pump power required is about 1 I.H.P. per 1000 feet of oxygen produced per day, the ratio decreasing for larger plants.

It is necessary that the barium oxide should be as hard and as porous as possible, and this is best obtained by preparing it by igniting the nitrate. The nitrate fuses and decomposition soon commences with evolution of a mixture of oxygen and oxides of nitrogen. This action continues for about 2–3 hours, during which time the contents of the crucible remain in ebullition. A porous mass is then left, which is heated for another hour to complete, as far as possible, the decomposition. In this way a very hard but also very porous baryta is obtained.

This process was thoroughly practical and economical, and large numbers of plants were erected all over the world and worked successfully for many years. It was described in detail with illustrations of plant in the first edition of this dictionary (*see* also K. S. Murray, Proc. I. Mech. E. 1890, 131; Thorne, J. Soc. Chem. Ind. 1890, 246). Some plants are still working, but in the last few years the process has been largely superseded by the still cheaper liquid air process, which also produces oxygen of greater purity (v. *infra*).

Cost of production. It is very difficult to obtain data of the cost of production of oxygen under the earlier methods described, but the following figures probably approximate to the cost per 1000 cubic feet:—from chlorate 8*l.*–10*l.*, from pyrolusite 4*l.*–6*l.*; from sulphuric acid 2*l.* 10*s.*–3*l.* (probably higher when only the oxygen and not the sulphur dioxide is utilised); by the Tessié du Motay process 3*l.*–4*l.*; by the Brin process 7*s.*–12*s.* No authentic data of the cost of producing oxygen by dialysis or by solution in water are obtainable, but it would probably be *at least* as high as that by the Tessié du Motay process. In the Kassner process the cost depends largely on the amount realised by the sale of the caustic alkali, but would certainly be prohibitive for technical purposes. For cost by the liquid air and electrolysis processes, v. *infra.*

Properties.—The International Committee on Atomic Weights has now adopted O=16 as the standard of comparison for all atomic weights, and under this scale H=1·008 (1·0076 Morley). Oxygen is a colourless, tasteless, and inodorous gas, of sp.gr. 1·1056 (air=1): at 0° and 760 mm. pressure a litre of the gas weighs 1·429 grms. (1·42893 at 0° and 760 mm., and 0·29071 grms. at 1067·4° and 760 mm., Jacquerod and Perrot, Compt. rend. 1905, 140, 1542), and at 30 ins. pressure and 15·5° 100 cubic ins. weigh 34·206 grs. 1 grm. of oxygen measures 0·6997 litres and 1 lb. 11·84 ft. Oxygen also occurs in an active allotropic form called *ozone*, which is treated of in a separate article (*v.* OZONE).

Oxygen normally acts as a divalent element, but in many compounds, especially in many organic compounds having somewhat basic characteristics, acts as a tetrad. When examined through very thick and highly compressed layers, gaseous oxygen has a slight blue tinge of colour. It is sparingly soluble in water. As with all gases, the quantity of oxygen dissolved by water depends on the tension of the oxygen in the atmosphere in contact with the water. Thus pure water shaken up in contact with pure oxygen will absorb nearly five times as much oxygen as it would when shaken up, at the same temperature and under the same pressure, with air—which only contains 20·9 p.c. by volume of oxygen. The following table gives the coefficients of solubility (*i.e.* the volume of oxygen absorbed by one volume of water when shaken up with pure oxygen under 760 mm. pressure) at different temperatures as determined by different observers :—

Temperature	Coefficient of solubility					
	Bunsen (1855)	Dittmar	Roscoe and Lunt	Winkler (1861)	Bohr & Bock (1891)	Fox (1905)
0°C.	0·0411	—	—	0·0489	0·0496	0·0492
10°	0·0325	0·0383	0·0377	0·0380	0·0390	0·0384
20°	0·0284	0·0312	0·0308	0·0310	0·0317	0·0314
30°	—	—	—	0·0262	0·0268	0·0267
40°	—	—	—	—	0·0233	0·0233
50°	—	—	—	—	0·0207	0·0209

These numbers multiplied by 1000 give at once the number of c.c. oxygen absorbed by a litre of water from pure oxygen.

The older numbers of Bunsen appear, from the results of more recent observers with more delicate apparatus, to be rather too low. Winkler gives the following formula for calculating the coefficient of solubility (β) of oxygen in water at any temperature (t).

$$\beta = 0{\cdot}04890 - 0{\cdot}0013413t + 0{\cdot}0000283t^2 - 0{\cdot}0000029534t^3.$$

Fox (Trans. Far. Soc. 1909, [v.] 68–81) gives the formula :—

$$\beta = 0{\cdot}04924 - 0{\cdot}0013440t + 0{\cdot}000028752t^2 - 0{\cdot}0000003024t^3.$$

The coefficient of solubility of oxygen in alcohol at 0° is 0·2337; at 20° it is 0·2201 (Timofejeff), so that oxygen is much more soluble in alcohol than in water.

Nearly all natural waters contain oxygen in solution and can only be freed therefrom by prolonged boiling *in vacuô*. This dissolved oxygen, though small in amount, is the source from which fish obtain the oxygen necessary to sustain life.

The solubility of oxygen in sea water at 16° is about 78 p.c. of its solubility in pure water (Clowes and Biggs).

Oxygen, though long regarded as a permanent gas, was liquefied in 1877 by Pictet at a pressure of 320 atmospheres, and a temperature of −140°. Cailletet had a few days previously observed the formation of a mist due to liquefaction when oxygen at −29° under a pressure of 300 atmospheres was allowed to expand suddenly. Olszewski in 1883 showed that the *critical temperature* of oxygen (*i.e.* the temperature above which no amount of pressure will liquefy it) is −113°, the pressure needed to liquefy it at that temperature being 50 atmospheres, and this was confirmed by Wroblewski and by Dewar in 1885.

Liquid oxygen is a pale steel-blue transparent and very mobile liquid showing a clear meniscus (Dewar; Olszewski) boiling at −182·5° at 760 mm. pressure. When the pressure is reduced or removed, evaporation takes place so rapidly that a part of the oxygen is often frozen. Solidification takes place under 9 mm. pressure at −211·5° (W.), under 172 mm. at −219° (Dewar, Roy. Soc. Proc. 1911, 85, 589). This latter temperature is therefore the lowest obtainable by the evaporation of liquid oxygen. Travers, Sinter and Jacquerod (Proc. Roy. Soc. 1902, 70, 484) found the b.p. of oxygen to be −182·8° at 760 mm., −185° at 600 mm., −188·5° at 400, and −193·8° at 200 mm. Dewar obtained solid oxygen as a hard, pale-blue mass by cooling liquid oxygen in a spray of liquid hydrogen. Its m.p. is −219° under a pressure of 1·12 mm. The density of liquid oxygen is 1·1181 at −182·5°, 1·1700 at −195·5°, 1·2386 at −210·5°, and that of solid oxygen 1·4256 at −252·5° (Dewar) corresponding to the general formula (for liquid and solid) $d = 1{\cdot}5154 - 0{\cdot}00442T^\circ$ (where T°=absolute temperature). 781·8 volumes of oxygen at 0° and 760 mm. are contained in 1 volume of liquid oxygen at −182·5°. The latent heat of vaporisation of liquid oxygen varies with the temperature (Alt), at 760 mm. pressure (*i.e.* −182·5°) it is 50·97 cals., at −205° it is 55·5 cals. The specific heat between −200° and −183° is 0·347±0·014. The vapour density at −182° is normal. The refractive index of liquid oxygen is 1·2236. Liquid oxygen absorbs nitrogen readily, absorbing at −190·5° 380 times its volume, or 42 p.c. of its weight of gaseous nitrogen, the b.p. being thereby reduced to −188·8°. This was probably the cause of the discrepancies in the boiling-points given by the earlier observers. Liquid oxygen is a very perfect insulator, and is also comparatively inert in its chemical properties. Phosphorus, potassium, sodium, &c., may be immersed in it without any action taking place (Dewar).

When liquid oxygen is subjected to the action of strong light, and particularly of the ultra-violet rays, some of it is converted into ozone (Dewar). It is diathermanous, a non-conductor of electricity, but is strongly magnetic, its magnetic moment being 1 when iron is taken as 1000. The magnetic susceptibility of liquid oxygen at the freezing-point is 1·3 times as great as that of the solid. Its susceptibility is diminished or temporarily suspended by elevation of temperature. Oxygen is the least refractive of all gases; it gives a characteristic though not very strong absorption spectrum, but to obtain this it is necessary to view the source of light through great thicknesses of liquid or through the highly compressed gas. The spectrum first appears in the form of a number of fine lines, but as the pressure is increased or a layer of liquid oxygen is employed, it shows a number of broader and shaded dark bands, with almost complete absorption in the violet and ultra-violet. Six absorption bands have been observed, two in the red corresponding to the A and B Fraunhofer lines. The absorption spectrum of liquid oxygen is practically identical with that of gaseous oxygen. Oxygen shows a luminous spectrum in a Geissler tube containing a bright band in the red, two in the green, and one in the blue, but the spectrum varies under varying conditions.

The chemical activity of air depends upon the oxygen it contains, air being simply, in its chemical relations, oxygen diluted with nitrogen. Free oxygen, whether diluted with nitrogen or not, manifests considerable chemical activity, even at ordinary temperatures, this activity increasing with rise of temperature. There are only few elements—viz. fluorine, chlorine, bromine, iodine, silver, gold, platinum, neon, argon, and helium—which do not unite *directly* with oxygen. Most of the non-metallic elements unite with oxygen to form anhydrous acids. Of the exceptions, hydrogen forms a neutral oxide (water), whilst no oxides of fluorine, argon, neon, or helium have yet been obtained.

Phosphorus combines with oxygen at ordinary temperatures, as do also moist iron, moist lead, moist saw-dust, and many metallic compounds such as cuprous chloride, manganous hydroxide, ferrous hydroxide, &c. This oxidation at ordinary temperatures is called *autoxidation*, and substances undergoing autoxidation often induce the oxidation of other substances present which otherwise would not oxidise spontaneously. The alkali metals, especially rubidium, are especially active in this way. In many cases ozone is simultaneously produced. Light, and particularly sunlight, greatly assists oxidation by gaseous oxygen. Potassium and sodium are at once attacked by dry oxygen at ordinary temperatures, becoming coated with their respective oxides. The majority of metals remain bright under similar conditions, but many become oxidised when moisture is present. In some of the metals oxidised by exposure to air the first coating of oxide formed acts as a protective covering and prevents further oxidation, as is the case with lead. In others, however, the oxide first formed gradually becomes converted into a higher oxide and may then give up part of its oxygen to the metal in contact with it, and the oxidation is thus propagated through the mass of the metal. The rusting of iron is not a simple case of oxidation (*v.* RUST). Some metals which in their ordinary condition are comparatively inert towards oxygen combine with it readily at ordinary temperatures when they are in a finely divided state, offering a very large surface for chemical action. Thus lead or antimony when obtained by the ignition of their tartrates, and iron, nickel, cobalt, and copper, when reduced from their precipitated oxides in a current of hydrogen at a low temperature, all ignite spontaneously in contact with air or oxygen, and when in this finely divided state are therefore often termed *pyrophori*. Silver, gold, and platinum are not acted on directly by oxygen at any temperature. Some metals in a molten state absorb considerable quantities of oxygen which is given out again wholly or in part when the metal solidifies. 10 grms. of molten silver at 1020° absorb about 20 c.c. oxygen (*v.* Donnan and Shaw, J. Soc. Chem. Ind. 1910, 987).

Molten platinum and palladium also absorb oxygen. Heated at 450° silver gradually absorbs *occludes*) about 5 times its volume of oxygen, gold 35–45, platinum 65–75, and palladium about 500 (7 p.c. by weight). Platinum black absorbs about 100 times its volume of oxygen and palladium sponge 1000, of which the whole is not given up again below a red heat. Wood charcoal absorbs oxygen at ordinary temperatures—about 18 times its volume (Goldstein)—but this absorptive power increases enormously at very low temperatures. At −185° 1 c.c. absorbs 230 c.c. of oxygen with the evolution of 34 cals., and this action may be employed to produce an oxygen vacuum, the pressure being reduced to that of a Geissler tube (Dewar).

The activity of oxygen is increased greatly by increase of temperature, and with most substances (except under the conditions already mentioned) an initial heating is necessary to start free oxidation, the heat evolved during oxidation being then sufficient to maintain it. Thus iron heated to bright redness in an atmosphere or stream of oxygen takes fire and burns brightly. A mixture of oxygen and hydrogen may be kept at ordinary temperatures for any length of time without change, but if the temperature of any part of the mixture be raised to bright redness—either by the electric spark, by the presentation of a flame or by other means—ignition at once takes place with explosive force throughout the whole mass. Under certain circumstances, however, this combination may be effected at ordinary temperatures. Thus, if a piece of clean platinum foil be hung in the mixture, combination takes place gradually at ordinary temperatures. This appears to be due to the power possessed by palladium, platinum, and some other substances of condensing gases and especially hydrogen on their surfaces, the activity of the gases so condensed being thereby greatly increased. If platinum or palladium black or sponge is used instead of foil, the action is so much increased that the heat evolved in the combination soon raises the temperature of the metal to the ignition-point of the gaseous mixture, and ordinary combustion ensues. This effect has been taken advantage of in the *Döbereiner* lamp (named after the investigator who first noticed this property of platinum) wherein a piece of spongy platinum is suspended over a jet connected with an automatic hydrogen-generating vessel. When the tap is turned on, the jet of hydrogen becoming mixed with air and at the same time impinging on the spongy platinum, oxidation takes place rapidly, the platinum soon becomes red hot and ignites the jet of hydrogen. Similar effects are produced with oxygen (or air) and gaseous hydrocarbons.

Various substances which expose large surfaces to air (or oxygen) become gradually heated through slow oxidation or combustion, and, if the heat cannot get away, ignition eventually occurs. Thus oily or greasy woollen and cotton rags and refuse are capable of absorbing oxygen fairly rapidly, and if present in any quantity the heat produced may accumulate and cause spontaneous combustion, and this action is a not infrequent cause of fires in factories. A similar generation of heat and eventual 'spontaneous combustion' often arises from the storing of moist hay in hayricks, and from the storage of damp coal in ships or heaps. The allegation that the ignition of coal is due to the oxidation of pyrites has been disproved by the work of Richters and Lewes, who have shown that the heat is generated by the absorption of oxygen and its action on the bituminous constituents of the coal.

Dixon, Baker, Traube, and others have shown that even at high temperatures the presence of a trace of moisture is necessary for free oxidation (combustion), and that in *absolutely* dry oxygen, sulphur and phosphorus can be distilled, and carbon made red-hot without combustion taking place. A jet of burning dry carbon monoxide is even extinguished when introduced into pure and absolutely dry oxygen. The presence of the minutest trace of moisture is, however, sufficient to restore to oxygen its activity.

In ordinarily dry oxygen all substances which burn in air burn with much greater brilliancy, and many substances which do not burn in air burn vividly in oxygen. Thus iron, zinc, &c., if the ignition is started by a portion being raised to a white heat in an atmosphere of oxygen, continue to burn with great brilliancy and with the evolution of a very high temperature. The actual amount of heat given out during the complete oxidation of any substance is the same whether the combustion is slow or rapid, and is carried on in air or in oxygen. But it is quite different in regard to the temperature developed, this depending on the concentration of the heat, and so being higher the more rapid the combustion and the less extraneous matter is present to absorb the heat. Thus, when phosphorus is burned in oxygen, the temperature produced is very high, and the combustion takes place with dazzling brilliancy. The temperature of a hydrogen or a coal-gas flame burning in oxygen is very much higher than that of a similar flame burning in air. The temperature of a flame of hydrogen burning in oxygen is 2800°; of carbon monoxide 2600°; and of acetylene 3000°. These facts have been utilised in the construction of the oxy-hydrogen and oxy-acetylene blow-pipes for obtaining very high temperatures (v. *infra*). If coal-gas is substituted for the hydrogen, a very hot flame is still obtained, but the temperature is not as great as when hydrogen is employed. 16 grms. of oxygen combining with hydrogen to form water evolve 68,400 cals.

Oxygen is the only gas capable of supporting respiration, and forms the life-maintaining constituent of air. In the pure state it may be inhaled for a time with impunity, and acts as a mild tonic or exhilarant. But its long-continued respiration is harmful, feverishness and weakness being produced; and it becomes poisonous if breathed under pressure. Dr. Richardson kept a rabbit in an atmosphere of pure oxygen at a temperature of 23·9° for 3 weeks. It ate voraciously all the time, but became so emaciated from inability to assimilate new material fast enough to supply waste that it was found necessary to discontinue the experiment. At 7·2° the rabbit became speedily narcotised, and would have died had it not been removed. Richardson found that cold-blooded animals were very little affected by being introduced into an atmosphere of oxygen, whilst most warm-blooded animals (dogs, cats, guinea-pigs, &c., but not the rabbit) speedily showed strong febrile symptoms (Asclepiad 1887–89). Some observers have noticed very decided narcotic effects produced on animals under these conditions, but Richardson ascertained that this is due to the oxygen becoming vitiated by repeated inhalations. He found that when the same oxygen was used over and over again, although purified from carbonic acid, &c., by passage over caustic potash, sulphuric acid, &c., the animals became speedily narcotised, but that when a continuous stream of fresh oxygen was employed this was not the case. This 'devitalising' of the oxygen appears to be due to traces in the exhaled gases of some compound which is not removed by the ordinary methods of purification. The electric discharge very quickly re-vitalised the vitiated oxygen. Flesh was found to decompose more readily in devitalised than in pure oxygen. At low temperatures, and at very high ones, however, oxygen is decidedly narcotic in its effect.

But although in health the continued inhalation of nearly pure oxygen is detrimental, its use where the action of the lungs and heart is sluggish, as in cases of partial suffocation, of collapse in cholera, pneumonia, and other illnesses, is very valuable, and has been the means of saving many lives. Its use in cases of cyanosis, gout, diabetes, &c., has also been found advantageous. Wounds and sores are said to heal more rapidly in an atmosphere of oxygen than in air, and it has been largely used in this connection.

Methods of testing and estimation.—The readiest test is the property possessed by oxygen of moderate purity of re-kindling a glowing splint of wood, a property only possessed by one other gas—viz. nitrous oxide. When mixed with colourless nitric oxide gas, oxygen produces deep reddish-brown fumes of nitric peroxide, whilst nitrous oxide does not. Nitrous oxide is also much more soluble in water than oxygen.

White indigo absorbs oxygen rapidly, at the same time turning blue. For general purposes of estimation, however, one of the three following methods is generally used :—

1. A solution of cuprous chloride in hydrochloric acid (which is colourless) absorbs oxygen readily with formation of cupric oxy-chloride. The greenish-brown solution of this salt may be again reduced by keeping copper foil in it.

2. An alkaline solution of pyrogallol absorbs oxygen freely, forming a dark-brown liquid. Good results are obtained by mixing 45 c.c. of a 25 p.c. solution of pyrogallol (prepared by dissolving 60 grms. in 180 c.c. water) with 145 c.c. of 60 p.c. solution of caustic potash (prepared by dissolving 400 grms. ordinary stick potash in 300 c.c. water). 200 c.c. of this solution will absorb nearly two litres of oxygen, but it is better not to push the absorption beyond about 450 c.c. as then more or less carbon monoxide may be formed. Carbon monoxide is also sometimes formed when the percentage of oxygen in the gas being tested exceeds about 30 per cent. Clowes (J. Soc. Chem. Ind. 15, 170, 742) recommends the use of a very large excess of potash to prevent the formation of carbon monoxide. He advises 160 grms. potash dissolved in 130 c.c.

water, and 10 grms. pyrogallol added to the alkaline liquid.

3. Clean moist copper absorbs oxygen freely, but a skin of sub-oxide is rapidly formed over the copper, which prevents further oxidation. An ammoniacal solution of ammonium carbonate, however, readily dissolves this sub-oxide again, leaving the clean copper. To utilise this reaction for analysis a suitable absorption vessel is packed with fine copper wire and then filled with a solution composed of equal volumes of ammonia of sp.gr. 0·930, and of a saturated solution of commercial ammonium carbonate. When the gas in which the oxygen is to be estimated is introduced into the vessel and displaces the liquid, a large surface of clean copper is exposed, and the oxygen is rapidly absorbed. When the residual gas is removed, the liquid again fills the vessel and dissolves the sub-oxide of copper formed, leaving the copper clean for the next analysis. 200 c.c. of this solution will dissolve the oxide formed by the absorption of about 4 litres of oxygen, but it is advisable to renew it after the absorption of about 3 litres, as otherwise a good deal of a yellowish-brown precipitate (probably an ammonia-copper compound) forms which renders the renewal more troublesome. A little fresh copper wire must be occasionally added as that in the vessel gets used up.

For all these tests Hempel's, Orsat's, or Stead's apparatus (*see* ANALYSIS) answer well for all but the most delicate determinations. With these an oxygen determination can easily be made in 10 mins.

If the first method is employed, the gas after absorption must be freed from hydrochloric acid by means of potash.

The property of phosphorus of absorbing oxygen at ordinary temperatures is also sometimes used for analytical purposes, but this is not a generally convenient method. A hydrochloric acid solution of chromous chloride or an alkaline solution of ferrous tartrate may also be employed.

Applications of oxygen.—Oxygen has been used successfully to maintain the air in a respirable condition in places where it cannot be replaced, as in diving-bells, submarine vessels, &c. Its use has often been suggested in connection with the ventilation of large halls, theatres, &c., but the cost has hitherto proved too great for its adoption.

It is employed in conjunction with hydrogen or coal-gas to produce the oxy-hydrogen and oxy-coal-gas flames in which platinum can be melted, silver distilled, &c. One application of these flames is in the production of the Drummond or lime light where the intense heat of the flame is made use of to raise a lime cylinder to a white heat and thus obtain an intensely vivid source of light. The oxy-hydrogen and oxy-coal-gas blowpipe is also used for the brazing of metals, autogenous soldering, the blowing and manipulation of hard-glass apparatus, and for many other purposes where very high temperatures and local heating are required (*v.* also *infra*).

Oxygen is used for many purposes in the laboratory, and, as already mentioned, for some medical purposes. It has been found that the admixture of small proportions (up to 6 or 7 p.c.) of oxygen with nitrous oxide during anæsthetising with that substance prevents or reduces the tendency to convulsions experienced with pure nitrous oxide, without reducing appreciably its anæsthetic power. Johnson has shown (J. pr. Chem. [i.] 49, 148) that anæsthesia may be produced with nitrogen equally as well as with nitrous oxide, and that a mixture of nitrogen with 5–7 p.c. oxygen forms a very satisfactory anæsthetic, producing slight or no convulsions.

Oxygen has been applied in the purification of coal-gas from sulphur compounds. It is found that if from 0·5–1 p.c. of oxygen is added to the crude coal-gas before it enters the purifiers the reduction of the sulphur compounds to 8–12 grs. per 100 cubic feet of gas may be effected by lime alone, the use of oxide of iron or lime sulphide being unnecessary. If oxide of iron is used, its efficiency is increased. In any case the purifying space needed is lessened, the life of the purifying material is lengthened, and the luminosity of the purified gas is considerably increased. If lime is used for purification the fouled lime ('blue billy') has not the objectionable odour which it usually possesses (Valon, Trans. Gas. Inst. 1889, 41).

It has been found that if, during the bleaching of paper pulps and other materials with bleaching powder, oxygen in a fine state of division is introduced into the bleaching potcher, a great saving of bleaching powder is effected, the bleached fibre also being stronger in texture (Thorne, J. Soc. Chem. Ind. 1889, 83).

Pure oxygen is also advantageously employed in the oxidation and thickening of oils for varnish and linoleum purposes. The thickened oil is paler in colour than boiled oil, the danger is less, as only steam heat is needed, and the thickening, besides being much more rapid, is accompanied by increase of weight instead of by loss of weight as in the ordinary process of boiling. The use of driers is also unnecessary (Eng. Pat. 18628, 1889).

Oxygen is now sometimes used to hasten the maturing of spirits, the same effect being produced in a few hours or days by means of pure oxygen acting on the spirit in a finely divided state as occurs under the ordinary method of storage in casks in 2 or 3 years.

Proposals have been made to use a mixture of oil gas and oxygen as an illuminating gas (Tatham, Eng. Pats. 13763, 16138, and 16142, 1889). It was found that, if 15–30 p.c. of oxygen is added to an oil gas retorted at a low temperature from a heavy and crude petroleum, a gas of very high illuminating power and of good travelling properties is obtained. The gas is a perfectly safe gas, as about its own volume of oxygen must be added to a heavy oil gas before an explosive mixture is formed. The same inventor proposed (*l.c.*) to use carburetted oxygen as a motive gas for engines, &c. He claims that with properly constructed valves, &c., perfect safety is secured, and that the great expansive force of carburetted oxygen on ignition gives results far superior to those obtained in the ordinary steam or gas engine.

The use in the manufacture of vinegar of small quantities of oxygen to act as a stimulant on the mycoderma has been found to considerably increase the rate of acetification.

L. T. T.

The Production of Oxygen by the Liquefaction of Air.

Since 1902, the liquid air process for the production of oxygen has rapidly come to the front and with the single exception of the electrolytic method it is now the oxygen process almost exclusively employed for commercial purposes.

The separation of liquid air into its main constituents, oxygen and nitrogen, was a problem which for many years, prior to 1902, occupied the attention of physicists and chemists who have studied the practical production of extreme cold and the liquefaction of gases.

It was, however, not until 1895 that the first real step of importance was taken in the practical production of liquid air. In that year, Carl von Linde took out a patent (Eng. Pat. 12528. 1895) for an apparatus which marked a new era in the production of liquid air and probably the first serious step in the separation of its constituents.

It had been proved by Thomson (Lord Kelvin) and Joule that if compressed air were allowed to expand without doing external work there was a slight fall of temperature due to the fact that internal work must be done in such expansion. Linde first realised[1] that this cooling effect increased very rapidly as the temperature fell, and in his patent of 1895 he utilised the fact to make a most practical and effective air-liquefier. He took highly compressed air at ordinary atmospheric temperature and caused it to pass through a coiled copper pipe contained in a well insulated heat interchanger. so constructed that the air which was allowed to expand through a throttle valve at the lower end of the coil was then caused to pass back in a reversed flow through the interchanger in intimate contact with the external surface of the pipe, through which the compressed air was passing on its way to the expansion valve. The principle of regenerative cooling was thus established between the expanded and compressed air with a self-intensive cooling effect which continued to increase until the cold became so great that a portion of the incoming compressed air was liquefied and collected in the vessel. Linde employed no preliminary cooling of the air and by this simple construction of self-intensive counter-current interchanger, there is no doubt that he originated an air liquefying apparatus of much scientific value, although not perhaps of much direct commercial utility.

But in his 1895 patent, Linde did not aim merely at providing a simple method of producing liquid air; his real object was by liquefaction and subsequent fractional evaporation to separate its constituents in order to obtain oxygen of commercial purity. To do this, Linde relied on the fact that nitrogen being more volatile than oxygen the vapour from a liquid mixture of the two was richer in nitrogen than was the liquid itself. This process of fractional evaporation did not, however, prove successful. It was found by experiment that under the most favourable conditions in order to obtain a residue containing 50 p.c. of oxygen 70 p.c. of the liquid had to be evaporated, and that the further evaporation was carried the greater became the proportion of oxygen lost in the vapours. Thus in the end when the liquid approached the ordinary commercial standard of purity in oxygen its quantity had become so minute as to be practically valueless.

The following table, prepared by Linde from his own experiments, clearly shows how the composition of the liquid changes even under the most favourable conditions, viz. during slow or quiet evaporation.

Per cent. of liquid not yet evaporated.	Per cent. of oxygen in liquid.	Per cent. of oxygen in vapour coming off.	Per cent. of original oxygen still in liquid.
100·0	23·1	7·5	100·0
50·0	37·5	15·0	80·0
30·0	50·0	23·0	65·0
20·0	60·0	34·0	52·0
15·0	67·5	42·0	43·0
10·0	77·0	52·0	33·0
5·0	88·0	70·0	19·0

Between 1895 and 1902, many patents were taken out for the production of liquid air, and the separation of its constituents. Nearly all appear to derive their inspiration from Linde, the low temperature for liquefaction of the air being obtained in practically every case by his nozzle expansion self-intensive system, whilst fractional evaporation of the liquid was invariably the system employed for obtaining oxygen.

As a matter of historical accuracy it must be admitted that for the seven years following Linde's patent of 1895 no substantial progress was made towards the industrial separation of oxygen from liquid air. It was not until 1902 (Eng. Pat. 14111, 1902) that Linde himself took the final step which solved that problem and laid the foundation for what is to-day undoubtedly the cheapest and best process for the production of oxygen.

It has already been shown that to obtain oxygen from liquid air by fractional evaporation a serious loss was entailed of the very substance that the process was designed to produce. It was this difficulty which Linde solved in his patent of 1902 and he accomplished it by adapting to the treatment of liquid air the process of rectification long known and employed in the production of alcohol (*see* Alcohol). Linde himself regarded his 1902 invention solely as an addition to the method of obtaining oxygen from liquid air by means of fractional evaporation as described in his 1895 patent and he only claims it as such. By introducing a rectification column, however, on the top of his evaporation chamber he not only succeeded in arresting the oxygen which was formerly lost but actually employed it to form part of a continuous rectification process for the production of oxygen in a state of remarkable purity.

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[1] It is a coincidence in the history of invention that the Eng. Pat. 10165 of 1895 was applied for by an Englishman, Dr. William Hampson, a few weeks before Professor Carl von Linde took out his British Patent. Hampson's patent is held by some to anticipate Linde in this country although there is no question as to the priority of Linde elsewhere. The terms of Hampson's provisional specification are somewhat ambiguous and it is difficult to say how much credit should be attached to this publication. Full details of Linde's apparatus were made known before the completion of Hampson's patent so that unfortunately his claim to priority has to stand on his provisional specification alone.

The simplest form of the Linde Oxygen Separator as employed to-day embodies all the essential features of his 1902 patent, so that a brief description of the actual machine with special reference to the accompanying diagrams may be taken as describing all the important characteristics of the apparatus as set forth in the specification and claim of that patent.

Fig. 1 represents diagrammatically the sectional elevation of a Linde separator capable of producing large quantities of oxygen of 98–99 p.c. purity. The circular upper portion of the casing, which is of wood, contains in its centre the rectifying column A, whilst the base constructed of wood in the form of a hexagon contains the vapourising, or distilling chamber B. All clearance spaces are packed with sheep's wool or other suitable insulating material in order to prevent the penetration of heat from outside sources. *c* is the counter-current interchanger constructed in the form of a large copper spiral pipe and containing three small copper pipes *d*, one of which is enclosed in a larger pipe *e*, as indicated more clearly in the sectional diagram, Fig. 2. c_1 is an extension of the main spiral pipe to the top of the rectifying column A with a gas or vapour collecting funnel F projecting within the same. e_1 is an open funnel-ended extension of the pipe *c* at the top of the vapourising chamber B. The pipe coil d_1, shown in the vapourising chamber, is connected at one extremity with the small pipes *d*, contained in the counter-current interchanger. The other extremity of this pipe is connected with the inlet of the valve box G, to the outlet of which another pipe d_2 is connected as shown. This pipe is carried upwards and enters the rectification column near the top where it is fitted as shown with a rose end, the function of which will be explained later.

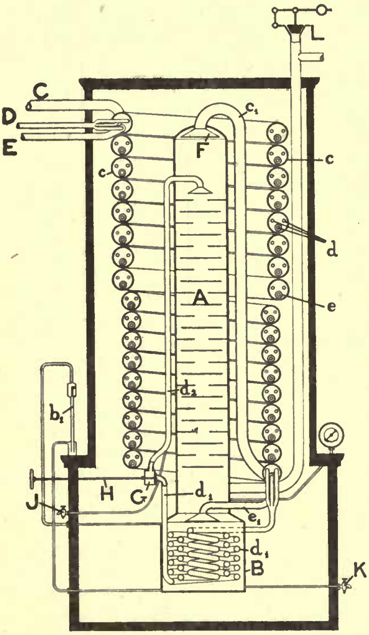

FIG. 1.

With this preliminary description of the essential parts, the working of the apparatus can now be readily followed. There are two stages in the working. *First*, the preliminary cooling down and production of liquid, and *second*, the separation of oxygen from the liquid.

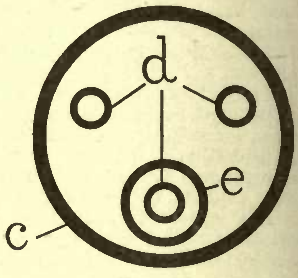

FIG. 2.

In commencing to work the machine, air at normal atmospheric temperature, or less, and at a pressure of about 2000 lbs. per sq. in. is conveyed from a gas compressor of suitable construction through the main pipe D, into the three small pipes *d* of the counter-current interchanger. It passes down these pipes and through the pipe coil d_1 in the vapouriser to the inlet of the valve box G. At this point, by the adjustment of the regulating valve spindle H, the air is caused to expand from a high to a low pressure and is discharged at this low pressure through the rose ended pipe d_2 into the top of the rectification column. This expanded air fills the column and then flows through the only two possible outlets, *c* and *e*, into the counter-current interchanger, in a reverse flow to the incoming high pressure air, leaving the apparatus through the pipes C and E as indicated.

It is at the valve G that Linde obtains the Thomson-Joule effect to which reference has already been made and regenerative cooling occurs in the counter-current interchanger where the incoming compressed air parts with some of its heat to the outgoing air which has been rendered colder by this temperature drop on expansion. The cooling effect throughout the whole apparatus goes on cumulatively until a temperature is ultimately reached at which the expanded air begins to liquefy and collect in that state round the coils in the vapouriser B. The quantity of liquid thus collecting is registered outside the apparatus by means of an ordinary coloured liquid which is contained in a glass tube b_1 enclosed in a pressure equalising circuit as indicated.

When the whole apparatus has been cooled down nearly to the temperature of liquid air, the liquid begins to accumulate rapidly in the vapouriser B, and the initial pressure of the air may be gradually reduced by increasing the opening of the valve G. Until this stage is reached, any separation of oxygen and nitrogen, which may have occurred, has been due simply to fractional evaporation.

As, however, the liquid begins to accumulate round the coil in the vapouriser B, the compressed air transmits some of its latent heat to the liquid. The latter is thereby evaporated whilst the compressed air is itself liquefied in proportion to the amount of heat thus extracted. The vapours thus produced begin to flow upwards through the rectification column in which the liquid air is flowing downwards. The temperature gradient necessary for efficient rectification then rapidly becomes established in the column and the second stage is reached in which the apparatus can be employed for the production of oxygen.

In the separation of oxygen from liquid air by rectification, Linde relies for his temperature gradient on the difference between the boiling-points of nitrogen and oxygen. The former is 77·5° absolute and the latter 91·5° absolute. Liquid air is discharged into the top of the column at a temperature of about 81° absolute. Nitrogen being the more volatile component it immediately begins to boil off, and thus automatically creates the maximum cold at the top of the column. For the same reason the nitrogen present in the original liquid collected in the vapouriser is the first element to be liberated by latent heat from the compressed air, so that the temperature of the liquid in the vapouriser becomes higher as its content of oxygen increases, thus the highest temperature is also established automatically at the bottom of the column. When all the nitrogen has been expelled from the vapouriser, liquid air passing down the column over various baffle plates comes into intimate contact with rising vapours of oxygen and an exchange of material takes place. At each stage some of the rising oxygen is condensed and some of the nitrogen in the downcoming liquid is evaporated whilst the liquid gradually gains in temperature until by the time it reaches the vapouriser its composition is that of practically pure oxygen. The gas, on the other hand, which passes off from the top of the column through the funnel F and the pipe c_1 to the counter-current interchanger, c, is mainly nitrogen at a temperature about 14° lower than that of the oxygen at the bottom of the column. The oxygen which rises in the column to effect the material exchange with the nitrogen of the liquid air is carried back to the vapouriser together with most of the oxygen contained in the original liquid. The excess of oxygen which thus continually gathers at the bottom of the apparatus is drawn off in a gaseous condition through the pipe e_1 into the pipe e of the counter-current interchanger. It will thus be seen that the gases drawn from the top and bottom of the apparatus are made to abstract heat completely from the incoming compressed air which is on its way to be liquefied.

The pressure at which the cold gases escape from the apparatus is from 4 to 5 lbs. per sq. in., just enough to cause them to pass freely through the counter-current interchanger. L is an emergency release valve on the low pressure system. J and K are test cocks communicating with the liquid air and liquid oxygen supplies respectively.

After the regular condition of oxygen producing has been reached the apparatus works steadily, the air supply from the compressor being kept at sufficient pressure not only to ensure its liquefaction at the temperature of the liquid oxygen bath (say 91° absolute), but also to ensure that the drop to the low pressure of from 4 to 5 lbs. sq. in. is sufficient to make good thermal losses due to leakage of heat from outside and to imperfect interchange in the counter-current apparatus. In practice, this pressure is found to be from 50 to 60 atmospheres.

A separate fore-cooler for the compressed air (not shown) is usually employed with the Linde apparatus. This fore-cooler is kept cold by means of a carbonic acid or an ammonia machine and is interposed between the air compressor and the separator so that the air leaving the compressor at normal atmospheric temperature becomes reduced to a temperature well below the freezing-point of water before it enters the separator. By this means, practically all the moisture which has not previously been abstracted by compression gets frozen out of the air. This is a point of more importance in actual work than the slight supplementary cooling which is obtained, because unless the air is thoroughly dry before it enters the coils of the counter-current interchanger the working of the apparatus is liable to be interrupted by the formation of ice which has to be thawed out before work can be resumed. This is an operation which involves considerable delay. It is usual therefore to make both fore-coolers and separators in duplicate to ensure continuous working. In addition to the elimination of moisture it is also desirable to remove carbonic acid from the air. This is usually done by drawing the air on its way to the compressor through a purifier containing slaked lime. In practice, separators work for a week or longer without freezing up and fore-coolers for about two days.

The three essentials of Linde's process could not be more concisely or accurately described than in his own patent specification. They are (1) cooling the air to be condensed in causing it to flow in the contrary direction to the evaporating products: (2) in then causing the same to transmit its latent heat to the evaporating liquid, and (3) in then causing the vapours produced in the distilling apparatus to flow upwards through the liquid flowing downwards in a stratified manner.

The first condition established the economy of the process by using the cold separated gases passing out of the apparatus to abstract heat from the incoming compressed air. It was by realising the possibilities of the second condition that Linde was able to achieve perfect rectification. Although the already cold compressed air is made to part with its latent heat while liquefying in the coils of the distilling apparatus its actual temperature cannot exceed that of the oxygen vapour which it has produced. By taking this liquid to the top of the column and letting it escape from a high to a low pressure the portion thus escaping undergoes an instantaneous partial volatilisation which, as already explained, reduces it so much in temperature that it can play the part of the cold member of the combination and thus establish the correct temperature gradient for the material exchange between liquid and vapour which the third condition renders possible.

The action which takes place in Linde's rectification column can be readily understood by reference to Baly's experiments on the 'Distillation of liquid air and the composition of the gaseous and liquid phases at constant pressure,' published in 1900 (Baly, Phil. Mag. 1900, 49, 517). It has already been shown (table, p. 45) how the composition of the liquid air changes during slow evaporation. Baly's experiments show that given any liquid mixture of oxygen and nitrogen equilibrium between its liquid and vapour is possible only where the vapour contains a definite proportion of the two constituents, but this proportion is not the same as that in the liquid.

The results in this direction obtained by Baly in a series of experiments are graphically set out in the diagram, Fig. 3, in which the ordinates indicate temperatures and the abscissæ percentages of oxygen. The curves indicate the composition of liquid and vapour respectively at definite temperatures. From these curves it will be seen that with vapours and liquid in equilibrium the vapours are always richer in nitrogen than their liquid. Thus when the evaporating liquid is liquid air (oxygen 21 p.c., nitrogen 79 p.c.), the proportion of oxygen present in the vapour coming off must be not less than 7 p.c. Although it is therefore possible by simple rectification as employed in Linde's apparatus to expel all nitrogen from the liquid by material exchange with the oxygen vapours, nitrogen itself can never contain less than 7 p.c. of oxygen. Whilst, therefore, the apparatus is capable of producing—and does produce—pure oxygen it is impossible to obtain nitrogen of equal purity without further treatment (*see* NITROGEN).

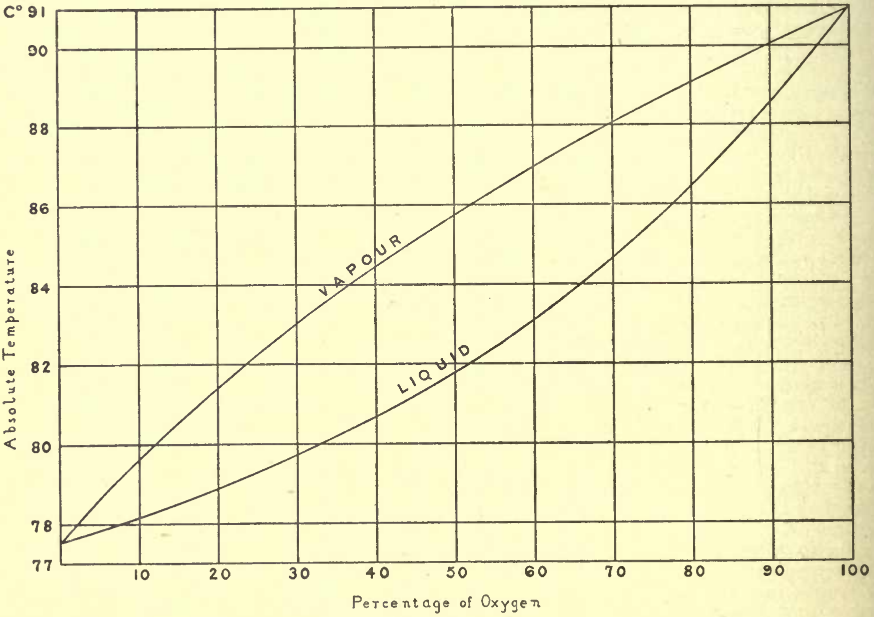

FIG. 3.

With the correct temperature gradient of the Linde rectification column it is easy to apply the conditions of the Baly curves. Starting with liquid air at the top of the column we know that 7 p.c. of oxygen must be present in the vapour given off. As the liquid descends it comes in contact with gas containing at each stage more oxygen than corresponds to conditions of equilibrium. Accordingly, oxygen is continually being condensed and nitrogen evaporated in the effort of the liquid to establish a condition of equilibrium with a vapour of constantly changing partial pressures, until ultimately at the base of the column pure oxygen is obtained.

Rectification, according to Linde's invention of 1902, although it yields pure oxygen, cannot be regarded as complete because, as explained, it leaves not less than 7 p.c. of oxygen in the waste gas.

A comparatively simple modification of the Linde process enables separation to be carried a stage further. This improvement is due to M. Georges Claude. Instead of condensing the compressed air integrally and then discharging it in one stream at the top of the rectification column, Claude employs a fractional method of liquefaction which separates the air on condensation into two liquids, one containing an excess of oxygen and the other an excess of nitrogen. The rectification column is made higher than that of Linde, and the liquid rich in nitrogen is discharged from the top, whilst the liquid rich in oxygen enters the column at a lower point appropriate to the proportion it contains of the two constituents. The additional scrubbing thus obtained with a liquid richer in nitrogen than air is the means of arresting a further 3 p.c. of oxygen without any additional expenditure of power. The waste gas consequently leaves the Claude apparatus with an oxygen content of only 4 p.c. Although

Claude's apparatus is somewhat more complicated to operate than that of Linde and requires more constant supervision, there is no doubt that this ingenious addition to the Linde process is of some practical value where large installations are concerned.

It may be mentioned here that although it has not been found possible by simple rectification to separate completely the components of liquid air so as to collect both the oxygen and nitrogen in a state of purity, it is possible by pushing Claude's system of fractional liquefaction a stage further to obtain small quantities of pure liquid nitrogen from an oxygen separator. This is done without expending any additional power, by a further fractionation of the liquid already rich in nitrogen. About 10 p.c. of the total nitrogen can thus, if desired, be obtained in a condition of purity the vapours being separately drawn off through the counter-current interchanger to a nitrogen holder. As the abstraction of this pure nitrogen from the liquid involves a somewhat higher percentage of oxygen in the rich nitrogen liquid supplied to the top of Claude's rectification column, it is obvious that the waste gas must also contain a somewhat higher percentage of oxygen, so that whilst pure nitrogen is being abstracted the normal yield of pure oxygen is appreciably diminished. The device is, however, a simple one which does not in any way impair the working of the separator when oxygen alone is required and as there is a small but growing demand for nitrogen in cylinders it is a profitable addition to the ordinary separator of an oxygen factory.

In the economical development of Linde's process, Claude is entitled to the further credit of being the first to utilise part of the energy contained in the compressed air by expanding it in a cylinder to perform external work. He thus obtains a greater degree of cooling than when Linde's system of nozzle expansion alone is employed.

Claude takes air from the compressor at a pressure of from 25 to 35 atmospheres, and after cooling it in the counter-current interchanger he expands it in the cylinder of his expansion engine to a pressure of 4 to 5 atmospheres. It then enters the separator where fractional liquefaction and ultimate rectification take place as already described. The power developed by the expansion engine can be absorbed in driving a dynamo or in any other suitable way, but the amount of energy recovered is so small that as an element contributing to economy in the production of oxygen it may be entirely disregarded. On the other hand, the fact that Claude can use air at an initial pressure of from 25 to 35 atmospheres as compared with Linde's pressure of 50 to 60 atmospheres indicates a total saving about 20 p.c. in power. In small plants (say up to a production of 20,000 cubic ft. of oxygen per 24 hours) this economy is probably quite counterbalanced by the additional complication and supervision involved. On the other hand, like Claude's addition to Linde's separator, his expansion engine becomes of practical value where large installations are concerned.

The Linde British patents were acquired in 1906 by the British Oxygen Company, Ltd., a concern which was founded as Brins Oxygen Company, Ltd., in 1886 (*v. infra*). From the end of 1907 until March, 1909, the Linde rectification patent was the subject of long and important litigation which resulted in it being unanimously upheld both in the Court of Appeal and the House of Lords.

The British Oxygen Company possess oxygen factories in London (2), Birmingham, Cardiff, Manchester, Sheffield, Newcastle-on-Tyne, and Glasgow. All of these are equipped with liquid air plants, including two on the Claude system (Claude's patents of addition having also been acquired by the Company). The total capacity of all the Company's oxygen plants at the present time (1913) is 400,000 cub. ft. per day of 24 hours, the quality of oxygen being as high as 99 p.c.

The cost of production varies considerably with the size of the plant. A plant to produce 40,000 cub. ft. of oxygen per 24 hours (which is a common size at the present time for a single unit in an oxygen factory) involves, in power, a total expenditure of about 100 b.h.p. Taking this at 0·35*d.* per b.h.p. hour, and adding all other direct charges, except depreciation and interest on capital, the cost per 1000 cub. ft. of oxygen into the holder works out at about 3*s.* 6*d.* The cost of such a plant complete with motive power, gas holder, and erection is approximately £7,500.

THE PRODUCTION OF OXYGEN BY THE ELECTROLYSIS OF WATER.

With the steady reduction in the cost of electrical power which has taken place in recent years combined with improvements in electrolytic apparatus, the production of oxygen and hydrogen from water by electrolysis has undoubtedly been established on a commercial basis.

Of the various processes employed to-day, the best known are probably those of Garuti, Schuckert, and Schmidt.

In all apparatus for the electrolysis of water, two essential conditions have to be observed :—

First: Reduction to a minimum of the electrical power required.

Second: Perfect separation of the two gases.

Water itself, as an electrolyte, is a poor conductor. It is usual therefore in all cases to render the liquid alkaline by the addition of 15 p.c. caustic soda or 20 p.c. caustic potash in order to improve its conductivity and thus facilitate decomposition.

Efficient separation of the two gases depends largely on the construction and arrangement of the electrodes and diaphragms, or partitions, employed in the voltmeters, or electrolysers, as they are more commonly termed, and it is principally in this respect that the various forms differ. Where diaphragms are employed, they should be permeable to the electrolytic solution, impermeable to the gases evolved, and they should be good conductors. Many porous materials, such as porcelain, pipe-clay, asbestos, plates of carbon, &c., have been employed, but all appear to have failed to realise satisfactorily one or the other of the requisites mentioned.

The objection at first to the use of metallic diaphragms was that they came under the influence of the electric current by induction from the electrodes. They thus acted to some extent as bi-pole electrodes, thereby creating a tendency for the two gases to be liberated in the same compartment, or cell.

Garuti discovered that if the electromotive force did not exceed 3 volts. and if the current was under 2 ampères per square decimeter of electrode, a metallic diaphragm remained passive, and he found that owing to its feeble resistance it was possible to work the apparatus with a difference of potential well under 3 volts. Garuti discovered, however, that it was necessary to carry the bottom of the diaphragm below the level of the bottom of the electrodes in the electrolyser in order to ensure this passive condition, and that this construction prevented good circulation of the electrolyte. He overcame the difficulty by perforating a large number of minute holes in the lower or immersed portion of the diaphragm. Whilst these holes permit the electrolyte to circulate they are practically impermeable to the gases.

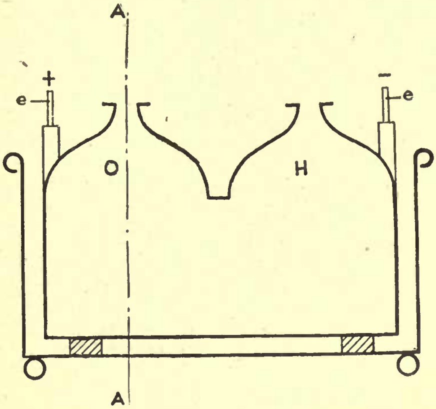

FIG. 4.

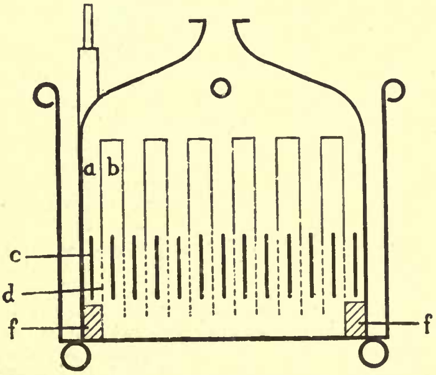

FIG. 5.

Figs. 4 and 5 illustrate diagrammatically a side elevation and cross section through AA of a Garuti electrolyser of this description. The outer tank in each is shown cut away.

The apparatus is composed of a series of alternate sheet steel compartments, or cells, *a b*, each enclosing an electrode *c* and consisting of long diaphragms *d* welded on to end plates and built up side by side. They are completely open at the bottom and the lower portion of the diaphragm is perforated as indicated. They are all open at the top for half their length, those containing an anode, or positive electrode (viz. *a*), being open to the left half of the figure and those containing a cathode, or negative electrode (viz. *b*), to the right half of the figure. In this way the collecting bell or cover welded on to the left portion O collects oxygen from the cells *a*, whilst the corresponding bell welded on to right portion H collects hydrogen from the cells *b*.

The anodes on one side and the cathodes on the other are welded to terminals *e* for the transmission inwards and outwards of the current. When the electrolysers are large the diaphragms and the electrodes are maintained rigid and equidistant by means of wooden partitions, or combs *f* placed at the lower extremity as indicated.

In the Schuckert electrolyser, the separation is effected with the aid of a metallic partition, or screen, between the electrodes, each of the latter being metallically suspended from the centre of a gas collecting bell which seats itself in the electrolyte so that the gas liberated round each electrode can be separately collected. The screen which is insulated from the metallic bells is carried into the electrolyte so far below the edges of the bells, containing the anodes and cathodes, that the metallic surface of the bells is practically unaffected by the current lines set up in the electrolyte. On the other hand, the bottom edge of each electrode is carried so far below the bottom edge of the screen that the gases generated at the respective electrodes can be obtained in a pure condition. The bells containing the electrodes and also the screens are independently constructed and may be multiplied in one electrolyser as desired.

Both the foregoing types of electrolysers, which indicate the general construction of such apparatus, work without any special supervision. They are usually made to produce from one half to two cubic metres of oxygen per hour and consequently twice that quantity of hydrogen. The electrolysers are placed in batteries side by side in a room which must be provided with excellent ventilation, or a ventilating fan, chiefly in order to obviate all risks through leakage, of explosive mixtures of the gases. In order to attain its full capacity the temperature of the electrolyte should be from 50° to 60°. The temperature of the room containing the electrolysers is therefore apt to become excessive unless adequate ventilation is produced. The requisite heat is generated and maintained in the electrolyte by its own decomposition, but steam heating is frequently provided and particularly when the electrolytic apparatus is arranged to work intermittently.

The gases produced under normal working conditions in a good electrolyser have the following degree of purity:—

Oxygen, 95–97 p.c.
Hydrogen, 97–99 p.c.

The impurities are mainly oxygen and hydrogen respectively and these residuals are largely eliminated by passing the gases through tubes containing heated palladium pumice on their way from the electrolysers to their respective holders. In the heated tube, the impurity in each case combines with some of the major gas in the form of steam, which is removed by condensation.

The first cost of a Schuckert electrolyser to produce ½ cubic metre of oxygen and 1 cubic metre of hydrogen per hour is given as about £75. Consequently for a plant to produce about 40,000 cubic feet of oxygen per 24 hours, the electrolytic apparatus alone, assuming current to be taken from an existing private source, or public supply, exceeds the cost of a liquid air plant of the same capacity *with power included*. If the first cost of the current generating plant be added to that of the electrolysers it is probable that the complete electrolytic installation costs more than double that of liquid air. It should, however, be pointed out that in smaller plants this difference in first cost is not so marked, whilst hydrogen, as the electrolytic by-product, is at present a more useful commodity than the nitrogen of liquid air.

The cost of decomposing water by electrolysis into its components, oxygen and hydrogen, is mainly a question of the electromotive force involved, and the consumption of energy under normal conditions can be readily calculated from existing data :—

One ampere decomposes 0·335664 grm. of water per hour, and liberates 0·037273 grm. of hydrogen and 0·29839 grm. of oxygen.

One litre of hydrogen weighs 0·0896 grm.

One litre of oxygen weighs 1·4300 grm.

Therefore in one hour an ampere liberates from water 0·416 litre hydrogen and 0·208 litre oxygen.

Calculated on Thomson's law, according to which the heat disengaged by the formation of water equals the E.M.F. necessary for its decomposition, it is found that 1·5 volts is the E.M.F. required. In practice, it is not possible to realise this theoretical result and it is admitted that an E.M.F. of not less than 2·5 volts s necessary.

The production of 208 litres of oxygen, alculated on this latter voltage, gives $\frac{\cdot 208 \times 1000}{2\cdot 5} = 83\cdot 2$ litres of oxygen per kilowatt our. Therefore, to obtain 1 cubic metre of xygen and 2 cubic metres of hydrogen exactly, 2·0 *kilowatt hours are required.*

Schuckert gives the consumption of energy with his electrolytic system as 12 to 14 kilowatt ours per cubic metre of oxygen. The manager f a large factory in Germany, employing Maruti's process, recently gave the present writer the figure of 13·5 kilowatt hours as his experience, and 15 kilowatt hours has been iven to the writer by other users of large lectrolytic plant.

An average of 14 kilowatt hours (say) 20 .H.P. hours, is consequently a reasonable stimate of power required in actual experience ith large plants for the electrolytic production f one cubic metre of oxygen and two cubic metres of hydrogen.

An electrolytic plant of the capacity which as been considered in the case of liquid air, iz. an output of 40,000 cubic feet of oxygen per 24 hours, requires therefore more than 9 times as much motive power as the corresponding liquid air plant. Assuming that current is drawn from a public supply at ½*d.* per unit (a price at which it can be readily obtained to-day in many places), the cost of energy per 1000 cubic feet of oxygen is 16*s.* 8*d.* Allowing 2*s.* 4*d.* to cover other direct charges, such as wages, material, current losses, renewal of plates, &c., and assuming the same depreciation and interest on capital, then regarded as oxygen producing processes, the respective figures of 3*s.* 6*d.* and 19*s.* may be taken as a fairly accurate comparison of the cost of production.

It is obvious therefore, that unless a ready market can be found for hydrogen, the electrolytic process cannot at present compete on equal terms with liquid air plants in the oxygen factory.

INDUSTRIAL PRODUCTION AND USES OF OXYGEN.

Prior to Linde's invention of 1902, oxygen for industrial purposes was produced by electrolysis, except in this country where the Barium Oxide process was for many years successfully employed by the British Oxygen Company. The Barium Oxide process must to-day be regarded as obsolete because, in first cost, quality of oxygen produced and cost of production it is quite unable to compete with Linde's liquid air process.

The electrolytic process, on the other hand, can at least supply a gas of equal purity, and where a useful outlet can be found for hydrogen the process can probably hold its own—particularly in cases where small private plants are required to produce oxygen in the works where it is to be consumed.

Three circumstances have, however, conspired in recent years to arrest development in the use of electrolytic apparatus for the production of oxygen. The first is the established success of the Linde process. The second is the introduction of oxy-acetylene welding which has not only largely superseded the older method of oxy-hydrogen welding but has in consequence created an extensive demand for oxygen, *per se*, thus detracting largely from the value of the hydrogen product on which the success of the electrolytic process mainly depends. The third is the low price at which oxygen can now be obtained in cylinders. This tends to restrict the sale of apparatus for private manufacture of the gas.

Undoubtedly the two most important industrial outlets for oxygen at present are oxy-acetylene welding and oxygen metal-cutting. Neither process has been before the public for more than six years, yet engineers have been quick to recognise the fact that each affords a valuable and economical method of dealing with an immense variety of metallurgical operations.

The increased demand for oxygen due to these developments has led to a very large increase in the number of oxygen factories.

In this country, besides the numerous extensions of the British Oxygen Company, to which reference has already been made, a number of electrolytic plants exist which produce oxygen either for private use or distribution in cylinders. In Germany, France, and Belgium, six years ago, there existed altogether about twelve oxygen factories nearly all employing electrolytic plants. To-day that number has been quadrupled by liquid air plants alone and a considerable number has also been installed in private works. Every country in Europe, except Portugal, has now one or more oxygen factories, and it is no exaggeration to say that all important engineering centres have practically unlimited supplies of oxygen available, in fact, the supply at the present time considerably exceeds the demand.

The total consumption of oxygen in Germany in 1911 was about 150,000,000 cubic feet. In France, it was about 100,000,000 cubic feet and in England about two-thirds that amount. 90 p.c. of the total consumption may safely be attributed—in about equal proportions—to welding and metal-cutting. The price of oxygen in cylinders for these industrial applications is about the same in each country and varies from ¼*d.* to ½*d.* cubic foot, according to locality and the quantity purchased.

In the United States of America, development has been slower owing to the dearth of oxygen factories. Five of these are, however, now in operation, equipped with Linde plants, and at least two other factories exist for the electrolytic production of oxygen. The oxygen industry is therefore certain to expand rapidly in America during the next few years.

In order to complete the list, it may be added that Linde oxygen plants, for the development of oxy-acetylene welding and metal-cutting, have been recently erected, or are in course of erection in Australia, New Zealand, South Africa, Egypt, India, China, Japan, Brazil, and the Argentine.

Oxy-acetylene welding. The temperature of the flame in a good oxy-acetylene blowpipe is approximately 3315° (6000°F.). This high temperature is mainly brought about by the combustion of carbon to carbon dioxide. Acetylene has a heating value of about 1500 B.T.U. per cubic foot. It is an endothermic gas approximately composed of 92·5 p.c. carbon and 7·5 p.c. hydrogen, which in combustion with oxygen form carbon dioxide and water In consequence of the high flame temperature, however, the water formed by this primary combustion is dissociated into hydrogen and oxygen, the latter element combines at once in the flame with the carbon of the acetylene to form carbon dioxide, whilst the hydrogen can only combine with oxygen which has passed out of the hottest zone of the flame, and thus does not involve a consumption of heat at the expense of the hottest part. It is, in fact, claimed for oxy-acetylene welding that the hydrogen forms a relatively cool jacket round the hot flame produced by the combustion of carbon in oxygen, and that as the hydrogen is not able to combine with oxygen at the very high temperature which exists within the inner zone, but remains temporarily in a free state, it protects the inner zone in a measure from loss of heat, whilst largely excluding the tendency to oxidation of the metal—a defect from which all other methods of welding suffer.

Theoretically, 2½ volumes of oxygen are required for the complete combustion of 1 volume of acetylene. In practice, however, with the oxy-acetylene blowpipe, it is found that the best welding results are obtained with 1·5 volumes of oxygen to 1 volume of acetylene.

The strength of the weld produced by the flame is almost invariably somewhat less than that of the original material. This may often be due to the use of welding strips of inferior tensile strength. It is, however, undeniable that the structure of the material in the weld is less homogeneous than in other parts. A good weld is largely a matter of skill on the part of the individual welder. It is possible for a competent welder, at his own discretion, to give a greater or less strength to the welded part, and for this reason it is impossible to draw conclusions from the work of one man as to the work of another. Oxy-acetylene welding must be regarded as a trade which can only be mastered by intelligent work and gradual development from simple to difficult jobs. Much depends on the intelligence and ability of the workman. A skilful welder will use a hammer freely as well as a blowpipe, more especially on vertical or overhead welds in plates which are subsequently to be subjected to pressure strains. By the judicious use of hammering at the right moment on the welded part the metal can always be made denser, with the result that the strength of the weld is increased.

The oxy-acetylene system of blowpipe welding is employed in two forms, which may be described as the high and low-pressure systems.

The first to be introduced was the high-pressure system, in which both gases are delivered to the blowpipe under pressure. Oxygen is supplied from an ordinary trade cylinder, and acetylene from a cylinder in which it is dissolved in a porous material soaked in acetone. Acetone has the property of absorbing 25 times its own volume of acetylene at atmospheric pressure, and it continues to do this for every atmosphere of pressure that is applied to the gas. This system affords an excellent and safe method of transporting acetylene and it supplies engineers with the means of using the oxy-acetylene blowpipe in its most portable form. It has many useful applications, and for repair work generally, but more especially on board ship, this system is admirably adapted.

The low-pressure system is almost exclusively employed for welding purposes in engineering works. In this latter method, only oxygen is required from a cylinder. Acetylene may be taken from any ordinary generator of approved design.

Oxygen has to be supplied to the blowpipes at a constant low pressure of from 5 to 30 lbs. according to the size of blowpipe employed. For this purpose the high and varying pressure of the gas cylinder is reduced to the constant low pressure required, by means of a pressure regulator which is attached to the cylinder. Acetylene (which must be well purified) is conveyed by any suitable system of piping from the holder of the generator to the place where it is to be employed. The blowpipes used are invariably of the injector type in which the oxygen under a suitable pressure is made to draw the necessary quantity of acetylene into the blowpipe and then deliver both gases well mixed and under sufficient pressure through the burner nozzle.

Fig. 6 illustrates a popular type of an injector blowpipe which, in addition to possessing all the usual characteristics of such a tool, is fitted with a head which can be adjusted as indicated to suit any special conditions of work.

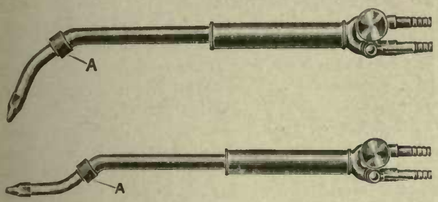

Fig. 6.

It is impossible to enumerate in detail all the work which may be executed by the oxy-acetylene blowpipe rapidly and economically, but the following are some of the applications for which it has already been advantageously employed:

The fusion welding of bicycle frames, forks, tee standards, wheel rims, &c.; the fusion welding of frames, wheel rims, &c., for motor cars; the repair of locomotive frames, &c.; in the manufacture of iron or steel motor or other boats as a substitute for rivets; the fusion welding of domestic and other hot-water boilers; the repair of steam boilers, boiler flues and other apparatus *in situ*; the fusion welding of steel or iron tanks, &c.; in the manufacture of safes; the fusion jointing of pipes of every description and shape for steam superheaters, &c.; the fusion welding of all joints in metallic casks, petroleum barrels, &c.; as a substitute for riveting in thin sheet ironwork, such as enamel ware; artistic ironwork; the repair of cracks, blisters, and flaws in iron and steel castings, forgings, &c.; as a substitute for brazing in many instances.

Metal cutting by oxygen. This process is based on the well-known fact that a jet of oxygen directed upon a previously heated spot of metal ignites it, with the result that the metal acting as its own fuel burns away rapidly in the form of metallic oxide.

In the year 1889, the late Mr. Thomas Fletcher, of Warrington, showed that, after heating an iron plate to incandescence by means of the oxygen and coal-gas flame obtained with one of his blow-pipes, it was possible, by largely increasing the supply of oxygen, to 'fuse' holes and even slots in the plate.

Twelve years later, the same process was applied practically by Dr. Menne, of Germany, to the opening up of tuyeres in blast furnaces which had become blocked by the solidification of metal.

The use of oxygen for this latter purpose proved so successful that its value in the cutting of metal was again suggested. Theoretically, once iron is ignited in oxygen, if a powerful jet of the gas is maintained in operation, it should be possible to burn away the metal without any auxiliary source of heat. Oxide of iron, however, is formed at a comparatively low temperature and lacks fluidity. It was found difficult in practice to eliminate all the oxide which was formed. Much of it adhered to the partially molten metal, thus preventing the intimate contact of metal and gas, with the result that combustion soon failed, and the cutting operation was arrested. The process was in consequence intermittent, the consumption of oxygen wasteful, and the cut wide, coarse, and irregular. In 1904, a cutting blowpipe, which is a very simple solution of this difficulty, was patented and subsequently introduced by the Société Anonyme L'Oxhydrique Internationale of Belgium. It consists essentially of an oxy-hydrogen, oxy-coal-gas or oxy-acetylene blowpipe, with an additional passage through which an independent and separately controlled stream of oxygen is supplied at the discretion of the operator. This separate supply of oxygen may be discharged through the centre of the blowpipe, in which case the mixed gases employed for heating are conducted through an annulus surrounding it, or the supply may be brought in a passage immediately behind the heating flame.

This simple expedient of maintaining an independent heating jet in operation whilst the cutter is travelling renders the cutting operation continuous. It furnishes the quantity of additional heat necessary to render the oxide fluid, so that it can be blown away through the cut by the separate jet of oxygen.

The cutting operation is very simple, and can be mastered by any intelligent workman in a few hours. The edge or surface of the plate at the point to be cut is first heated by the mixed jet of oxygen and any suitable fuel gas. When this spot has been brought to a state of incandescence, a fine cutting jet of oxygen is discharged upon it. This immediately produces combustion of the metal, with the resulting formation of iron oxide. The jet of oxygen is made sufficiently strong to blow away this iron oxide in front of it, with the result that a clean narrow cut is effected through the metal at a speed of travel which is comparable with hot sawing. The metal on each side of the cut is neither melted nor injured in any way, as the action proceeds too rapidly for the heat to spread; in fact the edges present the sharp and purely metallic surface of a saw cut.

The cutting may be made to follow any desired line, executing circles, curves, or profiles as desired, for which purpose guides and other mechanical contrivances are employed. Bevel cuts can be made and the process can be employed for the cutting of all grades or conditions of steel, as the action being chemical rather than mechanical the quality of the metal does not materially affect the results.

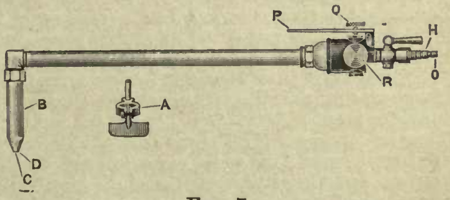

Fig. 7.

Fig. 7 illustrates a popular type of hand metal cutter, of the concentric type, in which the oxygen for cutting is discharged through the centre of the blowpipe whilst the mixed gases for heating are conducted through an annular passage surrounding it, all gas supplies being separately controlled.

Special appliances are supplied for ensuring a steady movement of the hand cutter, a matter of considerable importance where neat and accurate work is desired. In fact, machines and appliances are constantly being devised with the object of extending the applications of the process and of improving the results obtained.

The process may be employed for cutting sections of any thickness up to and even exceeding 12 inches, and the same cutter can be employed without any structural alteration on plates varying in thickness within wide limits: all that is necessary is to increase the velocity and quantity of oxygen used for cutting, to correspond with the increased thickness of the plate.

As indicating the remarkable possibilities of this process, the following results obtained in the cutting of nickel-chrome steel armour plate are interesting.

With a single jet of oxygen, a plate 9¾ in. thick was cut through at the rate of one foot in 3½ minutes with a consumption of 30 cubic feet of oxygen per foot run.

A plate, 12 in. thick, was cut through at the rate of one foot in 4½ minutes with a consumption of 50 cubic feet of oxygen per foot run.

Such results as these indicate the immense field of operation both in constructional and destructional ironwork which lies before this important application of oxygen. K. S. M.

OXYHAEMOGLOBIN *v.* Blood.

OXYLIQUIT. Liquid air mixed with oxidisable substances, such as wood charcoal. Used as an explosive.

OXYPHENINE (*Chlorophenine, Chloramine Yellow, Diamine Fast Yellow B, 2 F, etc.*) *v.* Primuline and its derivatives.

OXYPHLOROGLUCINOL *v.* Phenol and its homologues.

OZOKERITE, known in Germany also as *Erdwachs, Bergtalg, Bergwachs Fossiles wachs, Mineralfett, mineralisches Leischenwachs,* in Moldau also as *Zietrescit,* and in the neighbourhood of the Caspian Sea as *Naphtgil, Naphatil, Neftgil, Neftegil, Neftachil,* is a naturally occurring solid hydrocarbon of the olefine, or C_nH_{2n} series. Ozokerite is found chiefly in the Mioceneformation in Boryslaw, near Drohowycz, and in the region of Stanislawow, Galicia. The veins in which it occurs are 40 to 80 mètres deep, and 1 metre in thickness. They pass through beds of sand, from 8 to 10 mètres deep, containing large stones, and then through blue clay and a plastic loam. From this blue clay, naphtha usually springs. The centre of the basin is richest in wax; in some cases masses of such extent have been tapped that the miners have hardly had time to escape before the workings were filled with the plastic mineral. Such a deposit was found in the deepest shaft at Boryslaw, at a depth of 208 mètres (227 yards). In general, however, the yield of wax varies at from 4 to 8 p.c. of the mineral extracted. Ozokerite was discovered in 1833 by Dr. Mayer, in Slanic in Roumania, and Glocker, who analysed it in the same year, gave the mineral this name, deriving it from two Greek words meaning 'to smell' and 'wax.' It was discovered in Galicia by Doms in 1854. At first it was regarded as an unwelcome companion to the petroleum, as it frequently caused the timbering of the shafts to collapse. It was not until about 20 years later that this substance began to attain commercial importance, a method having then been discovered of producing from it a substance resembling beeswax and named ceresin.

In 1865, ozokerite, which had previously been regarded as a Crown mineral, was declared free, and the consequence was that a number of shafts were sunk in the district, and much speculation ensued. The land being parcelled out in small plots, the shafts were sunk in the immediate neighbourhood of each other, and much waste and danger ensued. In 1886, a law was passed, whereby the right of mining for ozokerite might be separated from the ownership of the land. In 1899, it was further enacted that shafts were to be at least 60 mètres distant from one another. The extraction is now carried out under official supervision. In nearly every case the mineral is raised through vertical shafts or pits over which a wooden roof is erected. The section of the shafts in the first instance is 4 square mètres (43 square feet); but, when the ozokerite formation is reached, an inner shaft 1 mètre square (10·76 square feet) is formed of timber, and the space between this and the timbering of the larger shaft is filled with a rich clay. This construction is adopted to exclude the surface-water, which is now kept down by machine driven pumps during the sinking. From the bottom of the shafts levels are driven into the ozokerite ground, the richer portions being raised and the refuse used to fill up the old workings. The softer parts of the marl are dislodged by means of pick or wedge; but where the rock is hard, and the permission of the mining authorities can be obtained, dynamite is used. The mineral used to be raised by hand in skips or tubs holding 40 to 50 kilos. (88 to 110 lbs.). But electricity has now been applied to the haulage and this has greatly increased the output, two men now being able to raise 120 skips of 135 kilos. per day where four men were needed to raise 60 skips of 50 kilos. in the same time. Modern methods of ventilation and electric light have now mostly replaced the hand ventilators and safety lamps formerly employed. The timbering of the shafts requires constant renewal and repairs; in some cases it is almost impossible to keep the shafts perpendicular.

The water is usually raised in tubs, and much difficulty is experienced in getting rid of it after it reaches the surface, on account of the numerous shafts and the broken nature of the ground. Costly modern pumping stations and machines have now been erected for this purpose. The mineral, when it leaves the tubs, is sorted by hand. The waste rock is picked out and tipped to spoil, lumps of ozokerite are specially selected, and the remainder of the rock, containing fragments of wax, is tipped into tanks full of water. On being well stirred, most of the wax rises to the surface and is skimmed off. The residue still contains from 2 to 3 p.c.

of wax. A more costly, but more thorough, method of separating the wax is sometimes employed. The mineral, after being hand picked, is tipped into cast-iron vessels, and water at 50° is poured over it. The tanks are heated gradually from below, until the water boils. At 60°–70°, the melted wax which rises to the surface is ladled off and poured into cold water where it solidifies, after which it is removed and the water contained in its pores removed by pressure. A further quantity of wax is obtained by stirring the remaining hot contents of the tanks. This process is known as Lep-boiling (Lepkochen) (J. Soc. Chem. Ind. 1892, 117; *ibid.* 1898, 236; Eng. Pats. 2242, 1890; 9781, 1891; Die Zeresinindustrie, by Bela Lach, 1911). The quantity of waste mineral being considerable, and the distance between the shafts small, a special railway has been built to remove the residues from the immediate neighbourhood of the mines.

It has also been attempted to extract the wax by means of solvents such as benzene, but only with very poor results. The wax so obtained is of a much lighter colour and higher melting-point (73°) than the ordinary kinds, but is, nevertheless, not so useful in the ceresin industry.

The annual production has varied from 4000 to 18,000 tons, and in certain years the value has exceeded 1,800,000 dollars.

The production of ozokerite in the Boryslaw district amounted, in 1887, to 96 p.c. of the total output in Galicia, and was valued at £152,900 (J. Shotsky, Allg. österr. Chemiker- und Techniker-Zeit. 1889, 614, 651; J. Soc. Chem. Ind. 1890, 597; *ibid.* 1892, 117; *ibid.* 1897, 774).

Since the production of ozokerite has become more costly, its output has decreased. Thus in 1904, Galicia, which practically supplies the whole world with the crude product, only produced 2908 tons.

The ozokerite forms lumps and layers from 3 to 9 decimètres thick, so that masses are often found about 100 kilos. in weight.

Other deposits of ozokerite are found at Truskawice, Starunia, Dwiniacz, Klecany, and Pruthale, always in Miocene formations.

It has also been found in Hungary by the river Iza in the neighbourhood of Pecora. Its quality here is similar to that in Galicia, but it has not been systematically worked up. In various parts of Roumania also, excellent ozokerite deposits exist which have not yet been exploited.

Ozokerite is found in the Caucasus, and among the Wasatch Mountains, Utah, about 173 miles east of Salt Lake City, America, where deposits of white ozokerite, miles in length, are said to be found.

Caucasian ozokerite resembles an inferior Galician variety. Melting-point of crude substance 68°. Treated with 20 p.c. of fuming sulphuric acid it yields 58·1 p.c. of second-quality ceresin; m.p. 68·5°; volatile portion, 1·8 p.c. The crude substance has a repulsive odour, is worked with difficulty in quantity, becomes stiff in the basin, and presses extremely badly (Lach, J. Soc. Chem. Ind. 1885, 488).

Rich deposits of ozokerite have also been found along the banks of the Kemioki near Tornea (J. Soc. Chem. Ind. 1901, 1043) and in the Island of Chelekon in the Caspian Sea (*ibid.* 1896, 932).

North American or Colorado ozokerite. Here extensive deposits of an ozokerite-like substance are found, the supply from which is hindered only by the transport difficulty. On being tested, however, the material seems to be of little use for the production of ceresin. It is supplied in cakes 36 × 20 × 6 cm. in dimensions. It is a dull black, hard substance, brittle and pulverisable, and smelling of catechu. Care must be taken in heating it, as violent frothing may occur from the presence of water.

The crude substance melts at 76·0°.

Treated by the above-mentioned process no ceresin is obtained. Even when heated to 300° it is impossible to filter it, although it is quite a thin fluid. Subjected to distillation it gives the following results:

	Per cent.
Paraffin oil	90·00
Gas	2·12
Water	2·60
Residue	5·28

It commences to distil at 360°, when nearly 3 p.c. of oil, solidifying at 30°, comes over. At a much higher temperature it distils steadily, giving a very fair crude product for paraffin extraction. This substance is apparently more suitable for paraffin-making than for the ceresin industry (B. Lach, J. Soc. Chem. Ind. 1889, 696).

In Utah, a dark brown ozokerite of m.p. 53°–55°, sp.gr. 0·9285, has been found (Seal, J. Franklin Inst. 1890, 100, 402; Parker, J. Soc. Chem. Ind. 1891, 736). Ozokerite is also found in Portuguese East Africa, in Ghazaland, and in many other parts of the earth, but generally either in too small quantities or of too poor a quality to make its extraction on a large scale profitable.

It varies largely in composition, in m.p. (56°–100°), in b.p. (210°–300°), and in sp.gr. (0·85°–0·97°), depending on its source. The native ozokerite is transparent, of a light-yellow colour, and of the hardness of beeswax. It smells like benzene or petroleum, but the harder varieties are almost odourless. The best ozokerite is yellow or greenish, and can be easily compressed between the fingers. This kind, however, is not much used for the preparation of ceresin. Ozokerite consists chiefly of heavy saturated hydrocarbons, together with unsaturated hydrocarbons and other substances (Gosling, J. Soc. Chem. Ind. 1898, 741; Israti, Chem. Zentr. 1897, i. 1222; *ibid.* 1904, ii. 1448; Fader, *ibid.* 1905, i. 1666; Morozewicz, *ibid.* 1909, i. 1113). It appears to have been formed by the oxidation and decomposition of the hydrocarbons of naphtha, since the action of oxygen on these compounds simply eliminates hydrogen. Thus, for example, naphthalene gives dinaphthyl and water:

$$2C_{10}H_8+O=C_{20}H_{14}+H_2O.$$

By further oxidation compounds are obtained of the formula C_nH_{2n}, which react with the hydrocarbons of the marsh-gas series, with formation of very complex carbon compounds of various melting-points, as for example:—

$$2C_8H_{18}+O_2=C_{16}H_{32}+2H_2O, \text{ and}$$
$$C_{16}H_{32}+C_8H_{18}+O=C_{24}H_{48}+H_2O.$$

According to this hypothesis, the formation of ceresin from naphtha by the oxidation of the compounds of the marsh-gas series, and the relationships of ozokerite, naphtha, and coal, can be explained in the simplest manner (Gosling, *l.c.*; Engler, Chem. Zeit. 1906, 30, 711; Künkler and Schwedhelm, Chem. Zentr. 1908, i. 1322; Rakusin, J. Russ. Phys. Chem. Soc. 1909, 41, 109).

The best kinds of ozokerite are used in the preparation of ceresin. For this purpose, the crude ozokerite is broken into small pieces and melted in tanks by the aid of steam coils. The mass is run into retorts and distilled with steam. When the distillate has cooled to an oily mass it is subjected to hydraulic pressure, after which it is again melted and treated with fuming sulphuric acid in vessels fitted with stirrers. A full description and figures of the plant and materials employed is given by Lach in his Zeresinfabrikation, 1911; *v.* also Gosling, *l.c.*). A number of methods of purification are also described in this work (*v.* also Marcusson and Schlüter, Chem. Zeit. 1907, 31, 348).

Good ceresin is not easily distinguishable from beeswax. The following are the best methods of discrimination—(1) Ceresin is not so easily kneaded between the fingers as beeswax, and is more brittle. A mixture of the two bodies cannot be recognised in this way. (2) Ceresin is almost unacted on by concentrated sulphuric acid, whilst beeswax undergoes perfect decomposition by such treatment. To reduce its cost and also to render it harder and more wax-like, ceresin is often adulterated with paraffin, rosin or colophonium, petroleum oil, or with carnauba and Japan wax.

In addition to the production of ceresin, ozokerite is used in the manufacture of candles, ointments, pomades, and shoe blackings. It is also employed to some extent in the manufacture of shining black paper and for the impregnation of certain kinds of wood in furniture manufacture.

Under the name of *okonite*, the residue remaining after the purification of ozokerite forms an excellent insulating material for electric cables (J. Soc. Chem. Ind. 1905, 518) and with an admixture of 50 p.c. India rubber, ozokerite is recommended as a very good insulating material.

Paraffin was formerly obtained from ozokerite by distilling the residue, forming ozokerite pitch.

Ozokerite vaseline is obtained by allowing melted ozokerite to pass through 12–30 filters of animal charcoal (depending on the degree of decolourisation required). The mass is then treated with superheated steam for 3–4 hours at 250° (Gosling, *l.c.*).

OZONE, or *active oxygen*. Sym. O_3; molecular weight, 48. Van Marum, in 1785, noticed that air or oxygen in the neighbourhood of an electrical machine, or through which a series of electric sparks had been passed, acquired a peculiar odour, somewhat resembling that of chlorine; and Cruickshank, in 1801, noticed a similar smell during the electrolysis of water. But Schönbein, in 1840, was the first to recognise that this smell was due to the formation of a new gas, to which he gave the name ozone (*ὄζω*, to smell). Shortly afterwards he found that ozone was also formed by the action of moist air on phosphorus. At first this substance was considered to be an oxide of hydrogen, but the researches of Marignac and De la Rive, of Andrews and Tait, of Fremy and Becquerel, of Brodie, and others, and especially of Soret, established the fact that ozone is an allotropic form of oxygen produced by the condensation of three volumes of oxygen into two of ozone; or, in other words, that, whilst the molecule of oxygen contains two atoms, that of ozone contains three. Its formation may be expressed by the equation $3O_2=2O_3$. One view held for some time was that ordinary oxygen was composed of negative oxygen, or *ozone*, and positive oxygen, or *antozone*, but the existence of the third form, or *antozone*, has been disproved.

Preparation.—As already stated, ozone is formed when a series of electric sparks is passed through oxygen or air, but the proportion of the oxygen so transformed is very small. A much larger proportion of ozone is formed when the silent discharge is substituted for the spark discharge, a contraction of the volume of air or oxygen occurring at the same time.

For this purpose a current of air or oxygen is passed between the terminals of an induction coil placed at a short distance apart and made as large in area as possible. The original Siemens 'induction tube' (1858) consisted of two concentric glass tubes, the outer tube being covered, the inner lined, with tinfoil. A current of air or oxygen is passed through the narrow annular space between the tubes, the metallic surfaces of the inner and outer tubes being connected with the terminals of an induction coil or electrical machine, and thus transformed into terminals of large area. A number of modifications of this apparatus have been employed. In some of these the metallic terminals are replaced by good conducting solutions, such as copper sulphate solution, &c., in others by shot, powdered graphite, &c., and the inner glass tube may be advantageously replaced by a metal tube. In many forms the terminals consist of flat metallic plates placed close together with a sheet of dielectric (glass, mica, &c.) between them, in others one or both poles consist of one or more points. Some inventors have claimed to get better results without the solid dielectric, relying only on the thin layer of air or oxygen between the plates as the dielectric. There is, however, little doubt that the solid dielectric between the electrodes is advantageous; on the one hand, acting as a condenser it increases the regularity of the discharge, and on the other, it very greatly reduces the tendency to sparking. But in all cases the principle is the same, viz. the passage of a current of air or oxygen between terminals of large area, placed very close together, and thus offering as little resistance as possible to the silent discharge and reducing sparking to a minimum.

More ozone is obtained when a current of oxygen is used than when air is employed. The proportion is also increased by thoroughly drying and cooling the oxygen, by increasing the pressure of the air or oxygen, and by bringing the terminals as near together as possible. Sparking is very detrimental, destroying much of the ozone formed. The best result is obtained when there is a continuous 'glow' discharge. If the air is moist, some nitric acid is almost invariably formed. Under favourable conditions, and when great care is taken to keep the temperature of the apparatus and gas low, about 25 p.c. of the oxygen may be converted into ozone; but ordinarily, or on the large scale, the proportion obtained is much smaller.

Briner and Durand (Compt. rend. 1907, 145, 1272), by immersing their ozoniser in liquid air at a temperature of −194° succeeded in converting 99 p.c. of the oxygen into ozone. In a bath of liquid carbonic anhydride and ether (−78°), only about 11 p.c. of the oxygen was converted. In the liquid air-bath the optimum pressure is about 100 mm., when the yield of ozone reaches about 55 grms. per kilo-watt-hour. As the pressure increases or decreases the yield decreases, being about 29 grms. at 255 mm., and 37 at 45 mm. Even at −194° the spark discharge only gives about 1 p.c. of ozone, and the authors suggest that even this amount is probably due to the action of the silent discharge simultaneously occurring. The authors found that under the conditions of their experiments very little heat was produced by the silent discharge, the evaporation of the liquid air-bath being hardly appreciably greater when the electric current was passing than when it was not.

The yield of ozone produced by the action of the silent discharge varies greatly under varying conditions, which will be considered later under the section *Industrial preparation.*

Schönbein noticed the formation of small quantities of ozone when phosphorus, partially covered with water, was left in contact with air. The phosphorus is oxidised to phosphorous and phosphoric acids, traces of ozone being formed at the same time, together with some hydrogen peroxide. According to Van't Hoff (Zeitsch. physikal. Chem. 16, 411) 4 atoms of phosphorus can cause the production of 1 mol. ozone. If the ozone remains in contact with the phosphorus it is soon decomposed again, as it oxidises more of the phosphorus. The best results are obtained by passing a rapid current of air through a tube or bottle containing moist phosphorus at about 24°, but the quantity of ozone formed even then is very small. The action does not take place at ordinary atmospheric pressure below 6°, and the optimum temperature is about 24°. Under reduced pressure the action still takes place at 0°. The addition of sulphuric acid and permanganate or dichromate to the water increases the yield of ozone. Dry phosphorus does not readily cause this reaction, but it is found that if the surface of the phosphorus is kept bright by occasionally fusing it, ozone is produced without the presence of water. Pure oxygen does not readily give this reaction unless its pressure is reduced. A mixture of oxygen with three or four times its bulk of hydrogen gives rather more ozone than air does, but the reaction is dangerous, as the phosphorus may become heated to the ignition point of the mixture and cause explosion. The slow oxidation of turpentine, oil of cinnamon, and many other organic substances, is also accompanied by the formation of traces of ozone.

The action of concentrated sulphuric acid on the peroxides of barium, sodium, hydrogen, &c., and on the salts of the per-acids at low temperatures yields oxygen containing small quantities of ozone. Potassium permanganate or dichromate give with strong sulphuric acid strongly ozonised oxygen.

If pure potassium chlorate is heated pure oxygen is produced, but if the ordinary commercial salt is used or manganese peroxide or another peroxide is added the oxygen evolved contains traces of ozone.

Crystallised periodic acid when heated at 130°–135° breaks up into water, iodic anhydride, and strongly ozonised oxygen (Rammelsberg), and aqueous solutions of the acid and of its sodium salt gradually acquire the smell of ozone.

Fluorine decomposes water and this reaction, especially at low temperatures, is accompanied by the formation of appreciable quantities of ozone, amounting sometimes to 10–12 p.c. (Moissan). If water is dropped into a tube of fluorine, deep blue vapours of ozone are evolved.

Malaquin (J. Pharm. Chim. 1911, [vii.] 3, 329) has described a new and convenient method of preparing small quantities of ozone. 20 grms. of ammonium persulphate are mixed with 15 grms. of nitric acid in a flask, the air displaced by carbon dioxide and the mixture then carefully heated to 65°–75°. The reaction, which is exothermic, then proceeds spontaneously, and, the resulting gas, after being freed from carbon dioxide by passing through weak potash solution, consists of 3–5 p.c. ozone, mixed with about 90–92 p.c. oxygen and 4–5 p.c. nitrogen. It is not advantageous to use larger quantities of the ingredients than the above, nor to increase the quantity of nitric acid.

The oxygen evolved at the positive electrode during the electrolysis of strongly acidulated water contains ozone when the anode is composed of a non-oxidisable material, such as gold, platinum, lead peroxide. But under ordinary conditions the quantity formed is very small, especially if the surface of the electrode is large. The quantity of ozone produced is increased by increasing the intensity of the current, by decreasing the surface of the anode, and by reducing the temperature. Fischer and Massenez (Zeitsch. anorg. Chem. 1907, 52, 202) used as anode a narrow platinum tube coated with glass with a narrow slit cut through the glass so as to expose a very small surface of platinum. The anode was kept cool by circulating through it a current of calcium chloride solution at −14°, and the electrolyte itself (sulphuric acid with five times its volume of water, *i.e.* just below the concentration of greatest conductivity) was kept at 0°. Under these conditions they obtained oxygen containing 28 p.c. of ozone by weight. Fischer and Bendixsohn (Zeitsch. anorg. Chem. 1909, 61, 13, 153), by embedding platinum foil in glass and grinding away the edge so as to expose a line of platinum of 0·01 mm. width, have obtained oxygen containing 23 p.c. ozone. Archibald and von Wartenberg (Zeitsch. Elektrochem. 1911, 17, 812) have found that in the electrolysis of dilute sulphuric acid the yield of ozone may be considerably increased when an alternating current is passed in addition to the direct current used for electrolysis. The alternating current apparently depolarises the electrodes, in consequence of which more of the atomic oxygen liberated at the anode re-combines to form ozone than under ordinary conditions. The authors found that of the anodic oxygen produced by the direct current, as much as 37 p.c. may be evolved in the form of ozone, although, owing to the large amount of gas produced by the alternating current, the content of ozone in the total anodic gas does not exceed 12 p.c. The electrolytic preparation is convenient for laboratory work, high concentrations being obtainable, but the consumption of current is large—out of all proportion to that consumed for the silent discharge method—so that there is little likelihood of its being commercially available.

The formation of ozone being a strongly endothermic reaction, Nernst (Zeitsch. Elektrochem. 1903, 9, 891) argued, from theoretical considerations, that at high temperatures oxygen should become self-ozonised, and that at 6640° oxygen must contain 10 p.c. of its volume in the form of ozone. Much experimental work was carried out to try and produce ozone by heat alone, but without success. However, Fischer and Braehmer (Ber. 1906, 39, 940), Fischer and Marx (*ibid.* 1906, 39, 3631; 1907, 40, 443), and Fischer and Wolf (*ibid.* 1911, 44, 2956), have proved the correctness of Nernst's views. The decomposition velocity of ozone at 1000° is so enormous that at that temperature 1 p.c. would be reduced to 0·001 p.c. in 0·0007 seconds. The only chance of obtaining the ozone formed at the high temperatures is, therefore, by cooling instantaneously, *i.e.* more rapidly than the decomposition velocity. This was effected by carrying on the heating or combustion in contact with liquid air or liquid oxygen. Flames of hydrogen, and acetylene of 1 c.m. length burning at the nozzle of a narrow quartz tube were plunged into and continued burning in liquid air or oxygen. Flames of CO and SH_2 could not be made to burn in the liquid oxygen, but were made to impinge on its surface. Burning sulphur and burning charcoal were thrown on to the surface of liquid oxygen. In all these cases ozone was obtained, the cooling effected by the liquid oxygen being more rapid than the rate of decomposition, the ozone formed was at once cooled and immediately dissolved in the liquid air or oxygen. When a glowing Nernst pencil at a temperature of about 2200° was plunged into liquid oxygen, ozone was produced, and when the experiment was continued for 10 hours nearly 4 p.c. of the oxygen was converted into ozone. Ozone was obtained when a current of oxygen or air was made to impinge on a glowing Nernst pencil in liquid air, or through a perforated pencil. With moist oxygen or with a fine stream of water hydrogen peroxide is also formed, and with air oxides of nitrogen are present. In the latter case, the slower the stream of air the more oxides of nitrogen are produced, the more rapid the stream the more ozone. With a stream of air of velocity above 30 metres per second ozone alone is produced, and below 5 metres per second only oxides of nitrogen. When an electrically heated platinum wire at 1700° was plunged in liquid air ozone was formed, but no nitric oxides. In liquid oxygen the platinum wire fused after disintegration, but by glazing it with zircon chloride or yttrium nitrate, the platinum wire lasted some minutes, and ozone was then produced. The arc light in liquid air produced ozone and oxides of nitrogen. In these reactions with air currents short heating and rapid cooling produced mainly ozone, long heating and slow cooling mainly oxides of nitrogen, and long heating and rapid cooling mixtures of ozone and oxides of nitrogen. In the combustion of hydrogen and of acetylene hydrogen peroxide was among the products. By varying the conditions the authors were able largely to control the formation of the various products. With the Nernst pencil in liquid air the action of the electric energy in the form of heat approximates to the same order of magnitude as it does in the silent discharge. A rapid stream of air or ozone blown diagonally against a Bunsen flame produces traces of ozone, and has been suggested as a technical method; but though the actual energy consumed in using high temperatures alone may not be excessive, the other conditions render its technical application hopeless.

The cathode rays and the ultra-violet light rays acting on air or oxygen produce ozone, and this action is much increased at low temperatures. If liquid oxygen is exposed to these rays ozone may be detected on evaporating the oxygen. If solid oxygen snow is dipped in liquid hydrogen and exposed to the ultra-violet rays, the oxygen, after evaporation of the hydrogen, is found to contain ozone (Dewar). The action of the ultra-violet rays in the sun's rays, on the upper layers of the atmosphere, is almost certainly one of the main causes of the ozone present in the atmosphere. But whilst the ultra-violet rays produce ozone from oxygen, they also have a destructive action on ozone already formed.

The rays emanating from strongly radioactive metals and their salts produce traces of ozone when acting on air or oxygen (Curie, Compt. rend. 1899, 129, 823).

Ozone is produced in minute quantities during the evaporation of water, especially when the latter is in the form of spray, and this forms one source of the ozone present in sea air.

Properties.—In almost all its modes of production ozone is mixed with considerable, generally with very large quantities of oxygen or air. In this diluted state it has a strong and characteristic odour, somewhat resembling that of dilute chlorine, and appears colourless unless viewed through layers of several feet when its blue colour becomes visible. The odour is distinctly detected in air containing only one part of ozone in 500,000 air. Hautefeuille and Chappuis (Compt. rend. 1882, 94, 1249) first succeeded in separating approximately pure ozone by carefully compressing ozonised oxygen to 125 atmospheres pressure at the temperature of liquid ethylene (−103°).[1] The ozone condensed as a deep blue liquid, the superincumbent highly compressed gas being also of a deep blue colour. Liquid ozone mixed with some liquid oxygen is obtained when a current of ozonised oxygen is passed into a tube placed in a bath of liquid oxygen. Ladenburg (Ber. 1898, 31, 2508 and 2830), by the careful fractionation of the mixture thus formed, obtained ozone of a purity of 84·4 p.c. When strongly ozonised oxygen is bubbled slowly through liquid oxygen in a tube, a mist gradually forms above the surface of the oxygen, and after a little while a dark blue drop of liquid ozone forms just above the surface (Dewar). On raising the tube a little this drop may be brought into contact with the liquid oxygen in which it immediately dissolves. Liquid ozone is a very deep blue, almost black liquid which is transparent in thicknesses of less than 2 mm., but above that thickness is almost opaque. The boiling-point was first given by Olszewski (Monatsh. 1887, 8, 69) as $-106°$. A careful re-determination by Troost (Compt. rend. 1898, 126, 1751) gave $-119°$. Liquid ozone is fairly stable at temperatures below its boiling-point, and may be distilled if contact with organic matter or other oxidisable impurity is avoided, but the least trace of such impurity causes violent explosion. The gaseous ozone formed by the vapourisation of the liquid is dark blue in colour and is very unstable, exploding violently on a slight rise in temperature or by contact with a trace of organic matter or easily oxidisable substance. As is natural in a strongly endothermic compound the gas gradually undergoes spontaneous decomposition. Very varying statements have been made as to the decomposition of ozone in admixture with air and oxygen, owing, in many cases, to the presence of traces of impurities in the samples tested, but the recent researches of Chapman and Jones (Chem. Soc. Trans. 1910, 97, 2463; 1911, 99, 1811) have cleared up the doubtful points. The decomposition, which is very slow at low temperatures, is greater the more ozone is present, increases rapidly with rise of temperature—at 100° from about one-half to three-quarters is destroyed in half an hour—and is almost instantaneous at 300°. The decomposition at high temperatures is accompanied by phosphorescence, which is very marked when a hot glass rod is brought near the surface of liquid ozone (Beger, Zeitsch. Elektrochem. 1910, 16, 76), and Dewar has noticed phosphorescence when passing ozone vapour through a capillary opening. The presence of oxygen, nitrogen, carbon dioxide, and moisture are practically without influence on the rate of decomposition, but the presence of traces of oxides of nitrogen, chlorine, phosphorus pentoxide, &c., very considerably accelerate it. Reduction of pressure also increases the rate of decomposition.

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[1] During compression care must be taken to keep the temperature from rising much, as otherwise the ozone is liable to explode with great violence.

Ozone is decomposed in unlimited quantity by the peroxides of manganese, cobalt, nickel, and lead, by the oxides of copper and iron, and also by silver leaf, the oxides or silver undergoing no permanent change. These effects are probably due to the successive or simultaneous formation and decomposition of higher oxides. In the case of silver leaf the alternating formation and decomposition of silver oxide may be observed. In some cases ozone acts, like hydrogen peroxide, as a deoxidising agent on highly oxidised compounds. Thus hydrogen peroxide is reduced to water, and barium peroxide to the monoxide. In these cases the ozone is simultaneously decomposed: $O_3+H_2O_2=2O_2+H_2O$. Ozone is also decomposed when agitated with powdered glass, or by passage over spongy platinum or palladium. It is, however, without action on permanganic or perchromic acids.

Very varying statements are made as to the solubility of ozone in water, some observers stating that it is insoluble. It is undoubtedly somewhat soluble, although the degree has not yet been satisfactorily determined. Various causes are probably contributory to these discrepancies. The tests have generally been carried out with very dilute mixtures, and the experimental figures so obtained multiplied up to correspond to pure ozone. The experimental error is thus very largely increased and is further augmented by the partial decomposition of the ozone during the tests, the very great variation in solubility at varying temperatures and possible deviation from the law of solution according to partial pressures. From some of the most trustworthy results it appears to be at least ten times as soluble in water as oxygen is. Thus Carius found the coefficient at $1°=0{\cdot}834$, Schöne at $18°=0{\cdot}366$, and McLeod at $14°=0{\cdot}274$. Mailfert (Compt. rend. 1894, 119, 951), working with an air containing 3–5 p.c. by volume of ozone, gives the coefficient of solubility as 0·64 at 0°, 0·5 at 11·8°, 0·27 at 27°, 0·03 at 55°, and 0·0 at 60°. Ladenburg, on the other hand (Ber. 1898, 31, 2510), gives the solubility as 0·01 by volume. The solution acts as a powerful oxidiser, and has the characteristic odour of ozone. The ozone in solution gradually disappears, and simple agitation of ozonised oxygen with water destroys much of the ozone.

The so-called ozone water of commerce generally contains no ozone, its activity being due to hypochlorites, nitrous acid, &c.

Ozone is a very strong oxidising agent, giving up one-third (one atom) of its oxygen very readily. Thus it converts copper, mercury, silver, iron, and most other metals into the corresponding oxides, but this reaction appears to require the presence of traces of moisture. Only gold, platinum, and some other metals of the platinum group are unattacked. Ozone has a remarkable effect on mercury, one bubble of oxygen, containing $\frac{1}{50}$ of its bulk of ozone, being sufficient to alter the physical condition of several pounds of mercury. The mercury loses its mobility, convexity of surface and lustre, and adheres to the surface of glass. If the ozone is moist, permanent oxidation takes place, but if perfectly dry the mercury is said to recover its usual physical properties when exposed to dry air. Ozone oxidises lead sulphide to sulphate, ferrocyanides to ferricyanides, manganous to manganic compounds.

Moist ozone oxidises phosphorus, sulphur, selenium, tellurium, and arsenic to phosphoric, sulphuric, selenic, telluric, and arsenic acids respectively, ammonia to nitrous and nitric acids, and silver and lead to their peroxides. Ammonia is oxidised to ammonium nitrite and nitrate, and hydrochloric, hydrobromic, and hydriodic acids are oxidised to water and the free halogen. Traces of ozone hinder the combination of hydrogen and chlorine, and traces of chlorine hinder the formation of ozone by the action of the silent electric discharge. It liberates iodine from potassium iodide, the potassium being converted into the hydroxide

$$2KI+O_3+H_2O=2KOH+O_2+I.$$

This reaction forms one of the best means of determining the amount of ozone in a gas, as the iodine liberated can readily be estimated by titration. But in large excess ozone, in presence of the alkali, oxidises some of the iodine to form iodite, iodate, and even periodate (Garzarolli-Thurnlackh, Monatsh. 1901, 22, 455).

Ozone oxidises most organic compounds, destroying caoutchouc and vulcanite, for instance, so readily that these cannot be used for making connections in its preparation. It bleaches most vegetable colouring matters (indigo, litmus, &c.), and decolourises blood.

In most of the above oxidations the volume of the gas remains unaltered, the molecule of ozone giving up one atom of oxygen to the substance and leaving a molecule of oxygen: $Cu+O_3=CuO+O_2$. Turpentine, oil of cinnamon, and many other essential oils, however, absorb the ozone molecule as a whole, and the reaction has been utilised to determine the composition of ozone. Thus, if a carefully measured quantity of dry oxygen is ozonised, the contraction carefully noted, and then the resultant gas shaken with turpentine, the ozone is absorbed with a further contraction, twice as great as the first, the remaining gas being oxygen. This points to the contraction of three volumes of oxygen to form two of ozone, and this result has been confirmed by Soret and others, who also determined the relative rates of diffusion of mixtures of ozone and oxygen and of chlorine and oxygen. The molecule of ozone, therefore, contains three atoms of oxygen, one of which is easily liberated in the nascent state, and so forms a powerful oxidiser $O_3=O_2+O$. In certain cases of oxidation, however, the ozone molecule acts as a whole, no free oxygen being liberated. This, as originally noticed by Brodie, is particularly the case in its oxidation of gases, sulphur dioxide, for instance, being directly oxidised to sulphur trioxide $3SO_2+O_3=3SO_3$ (Riesenfeld, Zeitsch. Elektrochem. 1911, 17, 634).

Some unsaturated organic compounds containing double linkings absorb oxygen to form comparatively stable *ozonides* (*see* OZONIDES), but Molinari finds that compounds with treble linkings do not form these derivatives and proposes this reaction for distinguishing between double and treble linkings.

Hydrogen is not oxidised by ozone at ordinary temperatures, but is at 100°. Water is not directly converted into hydrogen peroxide. Carbon absorbs and decomposes ozone, but is not itself oxidised at ordinary temperatures.

Ozone acts on solid or strong solutions of potash at low temperatures to form an unstable brown compound, which is probably K_2O_4 (Baeyer and Villiger, Ber. 1902, 35, 3038); this may be looked upon as a salt of an *ozonic acid* $H_2O_4(O_3+H_2O=H_2O_4)$. On rise of temperature, or acidifying, oxygen and traces of hydrogen peroxide are formed, but no ozone. With lime water ozone produces a granular precipitate which is probably a peroxide. With acetylene ozone reacts with explosive force.

If gold or platinum plates are immersed in ozonised air or oxygen they are found to have become electro-negative to other similar plates. Copper plates show similar action, but to a very much less degree.

The great chemical activity of ozone and its unstable character are largely due to the fact that it is a highly endothermic substance, and thus gives out a great deal of heat on decomposition. The following are the most important determinations by various investigators of the heat absorbed in the formation of ozone from oxygen:—

Hollman, 1868	17,064 Cals.
Berthelot, indirect, 1876 . .	29,800 „
Mulder and v. d. Meulen, indirect, 1882	33,700 „
v. d. Meulen, indirect, 1882 .	32,800 „
v. d. Meulen, direct, 1883 . .	36,500 „
Jahn, direct, 1908 . . .	34,100 „
Kailan and Jahn, 1910 (Zeitsch. anorg. Chem. 68, 243) . .	34,500 „
Kailan and Jahn, 1910 (*ibid.*), decomp. by hot pt. wire . .	34,000 „

Ozone gives an absorption spectrum consisting of numerous lines, of which the two most characteristic (of wave length 609·5–595·5 and 577–560) lie close on each side of the D line. Chappuis (Compt. rend. 1882, 94, 858) mapped 11 bands lying between the wave length 628·5 and 444. Schöne (Zeitsch. anorg. Chem. 1894, 6, 333) observed 13 more or less intense lines. Ladenburg and Lehmann (Ber. Deut. physikal. Ges. 1906, 4, 125) noticed, in the spectrum of liquid ozone, a line in the red which only appears when about ¾ of the ozone is evaporated, and considered this as pointing to traces of a higher molecular modification of oxygen being present, indications of which are to be found in other characteristics of ozone. Hartley (Chem. Soc. Trans. 1881, 39, 60, and 111) found many of the dark lines of the solar spectrum to be due to absorption by ozone present in the atmosphere and considered the colour of the sky to be largely due to this ozone. Meyer (Ann. Physik. 1903, [iv.] 12, 849) confirms Hartley's results and conclusions.

Ozone is more magnetic than oxygen, the ratio of its specific magnetism to that of oxygen being greater than the ratio of their densities.

Oxozone. Various workers have suspected the presence in ozone of a still more condensed form of oxygen. As already mentioned Ladenburg came to this conclusion from his study of the spectrum of liquid ozone, and in conjunction with Goldstein obtained ozonides containing the group O_4. Harries (Zeitsch. Elektrochem. 1911, 17, 629), by evaporating a mixture of liquid oxygen and ozone through a series of flasks, found the sp. gr. of the gas in the first flask greater than that of the gas in the second, and that the gas in the first flask liberated more iodine from potassium iodide than corresponded to its sp. gr., whilst that in the second liberated the expected amount. He then found (Zeitsch. Elektrochem. 1912, 18, 129) that whilst, as has been generally stated, moderately ozonised oxygen may be passed through caustic potash solution and sulphuric acid without appreciable loss of ozone, this is not the case with very concentrated ozonised oxygen, at all events when the latter has been produced by the silent discharge with a high tension current. Working with a mixture containing 11–14 p.c. of ozone produced by an 8000-volt current of 10 per second periodicity, Harries found that 3–4 p.c. loss of ozone occurred when the mixture was bubbled through a solution of caustic potash and a further 2–3 p.c. if it was subsequently passed through sulphuric acid. He has further (Ber. 1912, 45, 936), in conjunction with some of his students, published the results of the action of the washed and unwashed ozone in the preparation of ozonides. He finds that butylene with the washed ozone produces the monomeric ozonide $C_4H_8O_3$ and the dimeric ozonide $(C_4H_8O_3)_2$, but that with the unwashed gas the mono- and dimeric oxozonides $C_4H_8O_4$ and $(C_4H_8O_4)_2$ are also produced (Evers). Treating tetrahydrobenzene in hexane with the washed ozone the solid ozonide $C_6H_{10}O_3$ is readily obtained, even without recrystallisation, whilst with the unwashed a mixture of the ozonide and the oxozonide is produced (Seitz). Caoutchouc similarly yields $C_{10}H_{16}O_6$ and $C_{10}H_{16}O_8$ (Hagedor). From these results there is no doubt of the presence of a compound O_4 in ozone, and under the conditions in which Harries worked, he considers that of the so-called ozone about one-third was really oxozone. It is probable that the greater liberation of iodine just referred to is due to oxozone acting in a different manner from ozone on potassium iodide.

Detection and determination. Ozone is most readily detected by means of paper moistened with a mixture of starch and potassium iodide. If ozone is present, iodine is liberated, and the starch paper coloured blue. This reaction, however, is also produced by nitrous and nitric acids, by chlorine, &c., so that it is not conclusive. A more conclusive test is to take a piece of neutral litmus paper and moisten half of it with a neutral solution of potassium iodide. If now this paper is subjected to the action of ozone the potassium iodide is oxidised and caustic potash formed, which at once turns the litmus paper blue. The turning blue of the part of the litmus paper not treated with the iodide would indicate the presence of any ammonia, which might otherwise be taken for ozone. Chlorine, nitrous acid, &c., if present, would form a neutral potassium salt, or would show an acid reaction. If, then, the untreated end remains the neutral purple whilst the iodised end turns blue, the presence of ozone is fairly conclusively proved. The litmus may be advantageously replaced by phenolphthalein or rosolic acid. Papers moistened with guaiacum or with tetramethylene-*p*-phenyldiamine, both of which are turned blue by ozone, are very sensitive, but, like iodised starch paper, are also similarly acted on by other oxidising agents. Arnold and Mentzel (Ber. 1902, 35, 1324 and 2902) recommend paper soaked in solution of benzidene or of tetramethyl-di-*p*-aminophenylmethane. The benzidene is coloured brown by ozone, blue by nitrous acid, blue and then red by chlorine, and gives no reaction with hydrogen peroxide, hydrocyanic acid, sulphuretted hydrogen or ammonia. The 'tetramethyl base' gives violet with ozone, straw-yellow with nitrous fumes, deep blue with Cl or Br and no reaction with hydrogen peroxide. The sensitiveness of the reaction is increased by adding a trace of acetic acid. For the quantitative determination of ozone the potassium iodide reaction is satisfactory. It is best to pass the ozone through the neutral potassium iodide solution and acidify before titrating, but some investigators prefer to acidify before passing the ozone. In either case it is essential that a large excess of the iodide solution should be present, as otherwise some oxidation of the liberated iodine may occur. Ladenburg (Ber. 1903, 36, 115) obtained satisfactory results by passing the ozone slowly through standardised sodium-hydrogen-sulphite and then titrating. If the presence of oxidising agents other than ozone is suspected, two estimations should be made, the one of the gas in question, the second after the gas has been passed through a tube, heated at 260° to destroy the ozone. The difference of the two tests gives the ozone present. The presence of oxides of nitrogen may also be detected by passing the mixed gases into liquid air. The ozone is dissolved whilst even traces of the oxides of nitrogen are at once solidified and may be filtered off.

The determination of the density of the ozonised air or oxygen has been used for measuring the amount of ozone present. Otto has designed a baroscopic apparatus for this purpose, and also a dilatometer for utilising for the same purpose the dilatation caused by decomposing the ozone at the temperature of boiling amyl benzoate (261°).

Ozone is present in minute quantities in the atmosphere. The maximum amount is certainly never more than 1 part in 450,000 of air. Its principal sources are probably the silent discharge from thunder-clouds and accompanying the flash discharge of lightning, the evaporation of water, and especially of saline waters, as in the sea foam, the action of some vegetable products on the air, and, perhaps, in the greatest degree the action of the ultra-violet solar rays on the atmosphere. Wurster found (Ber. 19, 3208) that ozone is also formed by the action of sunlight on clouds. When clouds are continually formed from above (*i.e.* in sunlight), all become laden with ozone, whilst when they are formed from below the upper layers are much more charged than the lower.

The ozone present in the atmosphere probably plays an important part in keeping the air pure and fresh and destroying the deleterious organic matter constantly passing into the atmosphere from decomposing flesh, animal exhalations, &c. In the open country, and especially by the seaside, ozone can always be detected, but in the air of large towns it is either absent or present in much smaller quantities. Richardson proposed (Asclepiad, 1887) the artificial production of ozone for the purpose of purifying the air of sick-rooms and even of towns, but it is only recently that this use has been practically introduced.

When present in the air in very minute quantities ozone is very advantageous to health, but if the quantity present is enough to cause a strong odour it is found to have a very irritating and harmful effect on the mucous membrane and the system, producing headache, influenza, &c. If the quantity present is large it becomes a strong irritant poison, causing acute inflammation, and leading to fatal results. Slightly ozonised air and oxygen is now sometimes used medicinally, especially in pulmonary complaints. Labbé has shown that ozone to the extent of 1 part in 20,000 may be inhaled for half an hour at a time without any ill-effects.

Industrial preparation and applications. In recent years the industrial preparation of ozone has been very greatly improved, and has developed into an important industry, which is still growing rapidly. Of all the methods of producing ozone, the only one which seems technically economical is that by the action of the silent discharge in air or oxygen. Starting from the original Siemens ozoniser innumerable modifications have been proposed, but these may be broadly divided into three classes, and only a few of the principal can be referred to here. The first class comprises those with smooth electrodes of large area either in the form of concentric cylinders or parallel plates. The second comprises those having one or both of the electrodes more or less pointed; and the third is a combination of the first and second classes, wherein the plate electrodes are so modified or roughened as to virtually transform them into a very large collection of points. The majority of the industrial ozonisers have either one or two sheets of a solid dielectric between the two electrodes, though in some the air or oxygen is alone employed as the dielectric.

As already stated, the yield of ozone varies enormously under varying conditions of character of discharge, form of electrode, quantity and potential of current, &c. These conditions, which are very complicated, have been studied by numerous investigators, especially by Warburg and Leithauser, who have published very exhaustive and important results of their experiments (Warburg, Ann. Physik, 1901, 5, 781; 1902, 9, 1286; 1904, 13, 470 and 1080; 1905, 17, 6 and 29; Ber. Deutsch. physikal. Ges. 1904, 209; Warburg and Leithäuser, Ann. Physik, 1906, 20, 734; 1909, 28, 1; Russ, Zeitsch. Elektrochem. 1906, 12, 409; Gray, Sitz-Ber. K. Akad. Wissen. Berlin, 1903, 1016; Harries, Annalen, 1906, 343, 334; Ber. 1906, 39, 3667; Askernasy, Technische Elektrochemie, 1910; H. de la Coux, L'Ozone et ses Applications industrielle, deuxième edition, Paris, 1910; de Kay Thompson, Applied Elektrochemistry, Macmillan, 1911). Reference to these researches must be made for details, only some of the general results can be summarised. If a point distant 1 cm. from a plate connected to earth is charged negatively to 7000 volts in air, a bluish light surrounds the point. On raising the potential a red brush appears separated from the blue by a dark space, the plate remaining dark. From a positively charged point a reddish light appears at a low potential and a brush develops as the potential is raised. Old points tend to lose the power of forming the brush discharge, giving a spark instead, but the brush reappears if a spark gap even of only 0·1 mm. length is introduced before the points. If an alternating current passes between a point and an earth-plate the positive brush is apparent, although by means of a revolving mirror it may be seen that the negative is actually alternately present. Between plates with solid dielectrics between them a uniform luminosity occurs with a high potential, a lower one tending to form brush discharges. As a general rule, other conditions being equal, the *yield* of ozone in proportion to the energy consumed is highest, the more the uniform luminosity can be maintained, and the lower the temperature. The highest concentration of ozone is obtained with negative points, the highest yield with positive points. For concentrations up to 4 grms. per cubic metre positive points and a high current are most economical, between 4 and 9 grms. per metre negative points and low currents (Warburg and Leithauser).

The production of ozone from oxygen by the silent discharge is accompanied by a simultaneous destruction of the already formed ozone to oxygen, the decomposition being greater the greater the quantity of ozone present and the higher the temperature. This, on the one hand, causes a limitation of the concentration obtainable, and on the other, a decreasing efficiency the higher the concentration. The technical standard of concentration is generally taken as grams of ozone per cubic metre of air or oxygen. The maximum concentrations obtainable technically are about 50 grms. with air and 150 with oxygen—the concentrations and yields, under like conditions, with oxygen are about three times what they are with air—but for technical economy much lower concentrations are used. The concentrations at present employed are generally from 1 to 4 grms. per metre, the lowest concentration being selected which is consistent with the satisfactory carrying out of the process in hand. The cost per unit of actual ozone produced (*i.e.* consumption of energy per unit weight of ozone) increases rapidly with increase of concentration—an increase of concentration from 2 to 12 grms. means a loss of efficiency of at least 25 p.c. This must be borne in mind in comparing costs of ozone given in published statements, as in some cases where very low costs are claimed, the figures are based on such very low concentrations that the ozonised air or oxygen so produced is of very little technical value.

Siemens and Halske ozoniser. This consists of an inner cylinder of aluminium and an outer one of glass. Six or eight of these are enclosed in an iron case which is filled with water, the water acting both as cooling water and as the one pole, the iron case being earthed and so charging the water. The aluminium cylinders are connected with one pole of the high-tension apparatus. The current used is 8000–10,000 volts, and about $\frac{1}{2}$ kilowatt is required for this unit.

Andreoli ozoniser. In this, which was one of the early practical forms of ozoniser, the plates consist of serrated bands of aluminium placed side by side with the points (17,760 in each unit) of each electrode facing one another and having a glass plate between the two plates.

Otto ozoniser. This consists of an iron cylinder through which runs an isolated rotating metallic axle on which are mounted a number of thin aluminium discs. The cylinder is connected with the one pole, the rotating axle with the other, and the discharge passes between the cylinder and the aluminium discs. No solid dielectric or cooling is used and the voltage employed is 80,000.

Tindal-de-Frize ozoniser. An iron half cylinder forms the one pole, and aluminium discs placed at right angles to the cylinder form the other. No solid dielectric is used and a voltage of 15,000–20,000 is employed. The whole is enclosed in a case, glass cylinders filled with glycerol being placed between the discs to prevent short circuiting or side discharges.

Abraham-Marmier ozoniser. In this apparatus large plates a metre square are placed in pairs with a metal case filling the space between each pair. A stream of water for cooling runs through each metal case, and these cases are alternately connected to the two high-tension poles. A current of 15,000–20,000 volts is employed.

Ozonair ozoniser. This apparatus, which is now used extensively in England and on the Continent, consists of two plates made of an aluminium alloy gauze separated by a dielectric plate of micanite. It is claimed for this apparatus that the raised parts of the meshes act as rounded points in facilitating the regular flow of the current and so avoiding sparking, and that the open character of the plates cause the air circulation to prevent undue heating and obviate the need for water cooling. Several of these pairs of plates are enclosed in a case to form a unit. The voltage used is 5000–8000.

Elworthy ozoniser. The electrodes consist of metallic spirals surrounded by glass tubes, and the inventor claims that the spiral arrangement of the electrodes increases the yield of ozone. He employs a voltage of 11,000–12,000.

Howard Bridge ozoniser. In this apparatus the plate electrodes are perforated with conical holes, the air or oxygen passing in through these holes. The inventor claims that in this way the air passes more completely into the zone of electrical action than when it is introduced at right angles to the direction of the current, as is usually the case.

Vosmaer ozoniser. This consists of a series of parallel tubes each of which contains at opposite sides of the inner surfaces of the tubes two electrodes formed of strips of metal supported on porcelain insulators so that their inner edges, serrated in the form of a saw, point inwards towards each other.

Gerard ozoniser. In this apparatus the electrodes consist of concentric metallic cylinders with dielectric cylinders of glass or mica between them. The dielectric cylinder is supported at one place only, and the electrodes are cut or split so as to allow for free expansion. The ozonisers are collected in groups of ten, and the inventor claims that very high potential currents can be used without sparking, and great economy in energy consumption thereby effected: he claims to obtain 100 grms. ozone per kilowatt-hour and to reach a concentration of 30 grms. per cubic metre (Bull. Soc. Belge de l'Electric. 1910, 449).

In the technical apparatus described the air may be drawn or forced through as is most convenient. When dry air is used and the temperature kept down, about 40–60 grms. of ozone per kilowatt-hour is obtained at a concentration of about 2 grms. per cubic metre. If oxygen is substituted for the air, about 120–180 grms. of ozone is obtained. At lower concentrations with a rapid air current somewhat higher yields are obtained, at higher concentrations with a slower current lower yields. From thermochemical considerations the theoretical yield of ozone should be about 1·2 kilos of ozone per kilowatt-hour, so that the actual yield at present is with air only about 5 p.c. and with oxygen 15 p.c. of the theoretical. It is very probable that higher efficiencies may be obtained by improved ozonisers.

Erlwein (Zeitschrift fur Sauerstoff und Stickstoff, 1911, 3, 143, 164, and 181) calculates from these figures that, including working expenses, interest on plant, depreciation and other charges, the cost of ozone, as it can now be actually technically produced from air, would be from 14*d.* to 22*d.* per kilo, from oxygen from 8*d.* to 11*d.* per kilo, to which latter figure has to be added the cost of the oxygen. This would compare very favourably with the cost of available oxygen from the oxidising agents usually employed.

At present by far the largest and most important application of ozone is in the purification of drinking water. De Méritens in 1886 showed that if a water infected with bacteria were efficiently agitated with ozone the whole of the bacteria could be destroyed. Experiments to apply this fact to the industrial sterilisation of water were carried out in 1891 by Fröhlich and Werner Siemens, and an experimental plant was soon afterwards erected at Martinikenfeld. The first installation on a large scale was erected in 1893 by Schneller, van der Sleen and Tindal, at Oudshorn, Holland, for treating water from the Rhine, which contained from 5000 to 1,000,000 bacteria per c.c. This was followed by an experimental plant at the Hygiene Exhibition in Paris in 1895, and by an installation at St. Maur, near Paris, to sterilise two million gallons of water from the Marne per diem, both being erected by Tindal. About the same time Siemens and Halske put up large installations at Paderborn and Wiesbaden. Extended tests made by the Pasteur Institute, the Koch Institute, the Berlin Reichsgesundheitsamt, and by others conclusively proved that even on the industrial scale complete sterilisation of water can be effected by ozone. The pathogenic organisms are readily destroyed, the most resistant bacteria, as in most other antiseptic treatments, being the *bacillus subtilis*, the presence of which is harmless. Even when the water was intentionally very strongly infected with septic bacteria—in some cases to the extent of more than a million per c.c.—purification was complete. It is essential that the ozone be brought into contact with every particle of water to be purified, and for this purpose various forms of sterilising vessels have been used. The forms first used by Siemens and Halske and by Abraham-Marmier, consisted of wash towers filled with stones down which water in a fine state of division flowed, meeting an upward current of ozonised air. Otto used an 'emulsifier,' based on the principle of the Korting injector, to obtain his mixture of ozone and water, and in the Tindal-de Frize system the ozonised air was forced into water, flowing down towers containing horizontal perforated baffle plates. In more recent plant various modifications and combinations of these methods have been employed. In the Ozonair plant an additional chamber is employed where the water is, by means of special nozzles, atomised in an atmosphere of ozonised air. The amount of actual ozone needed to insure certain sterilisation varies according to the character of the water, but averages about 2 grms. per cubic metre (220 gals.), *i.e.* in the concentration of 2 grms. per metre of air usually employed, a bulk of ozonised air equal to that of the water to be purified. It is essential that the water should be free from suspended matter, and if it is not it must be filtered previous to ozonisation. If the water contains dissolved organic matter this has a tendency to hinder sterilisation, and a larger proportion of ozonised air may be necessary. In the same way dissolved iron, which is oxidised and precipitated by the ozone, increases the quantity of the latter required.

Fresh installations have followed rapidly, and at the present time more than forty towns in Europe and America have adopted ozone purification of their water supplies. Amongst these are St. Petersburg (Siemens and Halske, 11,000,000 gals. per day), Nice (Otto 10,000,000 gals.), Florence (1,000,000 gals.), Philadelphia (Vosmaer, 1,000,000 gals. of water from the Schuylkill River, which is said sometimes to contain two and a half million bacteria per c.c., a large proportion of which are septic), and Lindsay, Ontario (Howard-Bridge, 1,500,000 gals.). At St. Maur two new installations are being erected, each to have a daily output of 10,000,000 gals., one having the Siemens-de Frise plant, the other the Otto-Abraham-Marmier. Hitherto there has been no similar plant in England, but the Ozonair Company have just completed an installation to treat the water supply of Knutsford, Cheshire.

The cost of sterilisation of water by ozone must vary according to conditions, size of plant, &c. For small installations it should not exceed one penny per 1000 gals. of water, and for large installations may be less than a halfpenny. The cost of each new installation at St. Maur for 10,000,000 gals. per day is to be £14,500, and from present working the engineer estimates that the cost of purification will be one-third of a penny per 1000 gals.

Portable ozone water purifying plants were used with success in the Russo-Japanese war, small plants for domestic supplies are now manufactured, and there is a small automatic plant obtainable which can be attached to the water supply tap. This consists of a modified Körting injector attached to the tap and connected with a small ozonising plant. The current is taken from the house supply, and the act of turning on or off the tap automatically starts and stops the process.

Another important application of ozone which has made great progress recently is for the purification of the air of rooms and enclosed spaces. It is now recognised that the bad effects of the close air of crowded rooms, &c., is not due to the excess of carbonic acid or of moisture present, but to the traces of various organic exhalations coming from the lungs and skins of the people and animals present. These traces of organic matter are readily oxidised by ozone, even when the latter is present in such minute proportions as to be harmless and even beneficial when breathed. It has been found that the introduction of small quantities of ozone into close air has the result of removing the 'stuffiness' and unpleasant effects, and making the air pleasant and invigorating. It has been said that it also destroys the bacteria present, but for any real bactericidal effect a concentration of at least 1 part by volume of ozone in 2000 parts of air is necessary, a proportion which could not be breathed. The fresh air from outside coming in through the ozoniser may very possibly be partially sterilised, and with the wall ozonisers where circulation of the air is caused, a part circulates through the ozoniser and may probably be partially sterilised. Large numbers of installations have been put into private houses, hospitals, theatres, and other public buildings, &c., and the process has just been adopted on a large scale for the purification of the air of the Central London Tube Railway. It has also been adopted with advantage in cold-stores, slaughter-houses, and factories or workshops where unpleasant smelling work is being carried on, for deodorising generally, and in Paris in connection with the disinfection of clothing.

As ozone can now be obtained at a moderate cost, has such active oxidising properties, and in oxidising introduces no foreign matter, it should find large application in the chemical industries. It has already been largely used in the production of vanillin by the oxidation of *iso*eugenol, one company making about 200 tons of vanillin per year in this way, and largely through this the cost has fallen from about £20 to £2 per lb.

Ozone is beginning to find applications for bleaching various substances, oils, fats, waxes, sugars, fabrics, &c. It is being used in the ageing of spirits and in leather curing.

Ozone is now being largely used in breweries with good results (Vetter, Woch. Brau. 1911, 28, 13, and 26; Vetter and Moufang, *ibid.* 1911, 28, 377). Passed through yeast the latter is greatly improved and strengthened, and the introduction of ozone into the air of fermenting rooms, refrigerator rooms, &c., keeps these sweet and clean. Vetter and Moufang claim its successful use for sterilising casks, pipes, &c., but this is controverted by Will and Beyersdorf (Zeitsch. ges. Brauw. 1912, 35, 73, and 89).

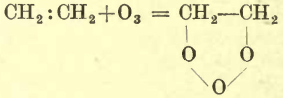
Ozone has been recommended and used for the bleaching of flour, &c., but it is not satisfactory for this purpose, acting detrimentally on the flour itself.

As already mentioned, ozone is now being considerably employed for medical purposes.

L. T. T.

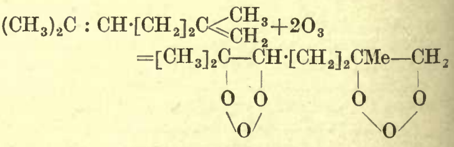
OZONIDES. The term ozonide was originally applied by Schoenbein to certain metallic peroxides which, when decomposed, yield ozone. Later, Bourquelot applied it to certain organic 'ozone carriers' (Chem. Zentr. 1897, ii. 45). The term is now used almost exclusively to designate the ozone derivatives obtained by the action of ozone on various classes of unsaturated organic compounds.

The reaction between ozone and an unsaturated ethylenic hydrocarbon may be represented by the equation



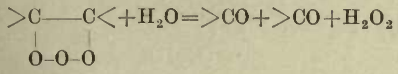
$$\mathrm{CH_2{:}CH_2+O_3 = \begin{array}{ccc} CH_2 & — & CH_2 \\ | & & | \\ O & & O \\ & \diagdown O \diagup & \end{array}}$$

and

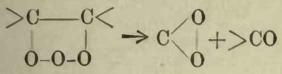


$$\mathrm{(CH_3)_2C : CH{\cdot}[CH_2]_2C{\lessgtr}^{CH_3}_{CH_2}+2O_3}$$
$$\mathrm{=\begin{array}{ccccccc} [CH_3]_2C & — & CH{\cdot}[CH_2]_2 & & CMe & — & CH_2 \\ | & & | & & | & & | \\ O & & O & & O & & O \\ & \diagdown O \diagup & & & & \diagdown O \diagup & \end{array}}$$

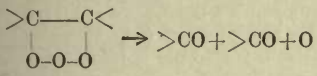
one molecule of ozone being added on for each ethylene linking. When heated or treated with water, these ozonides may decompose in various ways:

I. 

$$\underset{O-O-O}{>C-C<}+H_2O=>CO+>CO+H_2O_2$$

II. 

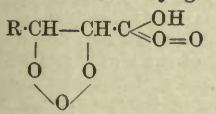
$$\underset{O-O-O}{>C-C<}\rightarrow C\genfrac{}{}{0pt}{}{O}{O}+>CO$$

III. 

$$\underset{O-O-O}{>C-C<}\rightarrow >CO+>CO+O$$

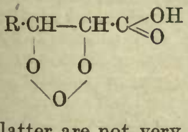
II. and III. take place both in the absence and in the presence of water, whilst I. only takes place in the presence of water; carbon di- and monoxide are usually found in the gaseous products, which shows that more complex decompositions also occur. Ozonides for a long time had not been isolated because of their ready decomposition by water, and in their preparation it is necessary to exclude all traces of water, otherwise these decomposition products and not the ozonides are formed. When caustic soda is present, the alkali tends to condense and resinify the aldehydes formed in the reaction, and acids are also formed.

The ozonides of aliphatic compounds so far known are not directly precipitated on ozonisation in chloroform, methyl chloride or carbon tetrachloride, but those of the hydroaromatic and other ring system hydrocarbons, almost always separate under these conditions, often even quantitatively as thick oils or gelatinous masses; substances containing conjugated double bonds only add on 1 mol. ozone quickly, but much stronger ozone and a more prolonged reaction are necessary to complete ozonisation. If the unsaturated substance also contains a carbonyl group, a perozonide is formed, an ozone molecule attaching itself to the unsaturated linking whilst one oxygen atom of another ozone molecule becomes attached to the carbonyl group thus:



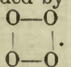
$$R\cdot\underset{O-O-O}{CH-CH}\cdot C\genfrac{}{}{0pt}{}{OH}{O=O}$$

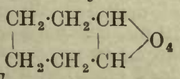
These substances have the properties of the ozonides and when treated with water or sodium bicarbonate often yield the normal ozonides



$$R\cdot\underset{O-O-O}{CH-CH}\cdot C\genfrac{}{}{0pt}{}{OH}{O}$$

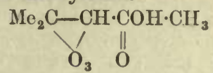
providing the latter are not very unstable.

Another class of perozonides is known, formed when a hydrocarbon ozonide is treated with more ozone; the oxygen atom in this case is taken up within the ozone molecule and the substances thus formed are regarded by Harries as being derivatives of oxozone  $\begin{array}{c}O-O\\ |\quad\;|\\ O-O\end{array}$. Thus the perozonide of cyclohexene



$$\begin{array}{l}CH_2\cdot CH_2\cdot CH\\ |\qquad\qquad\;\;|\\ CH_2\cdot CH_2\cdot CH\end{array}\Big\rangle O_4$$

would be called *cyclohexeneoxozonide*, whilst the perozonide of mesityloxide



$$Me_2\underset{O_3}{C-CH}\cdot\underset{\underset{O}{\|}}{COH}\cdot CH_3$$

would be termed *mesityloxideperozonide*. The oxozonides do not yield ozonides when treated with water; they are more stable than the perozonides and, when treated with more ozone, they may sometimes be made to combine with a fifth atom of oxygen. The constitution and structure of a large number of substances have been elucidated by the formation and subsequent decomposition of the ozonides.

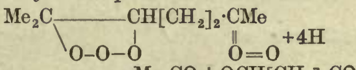
Compounds containing acetylene linkings also form ozonides quickly with concentrated ozone, slowly with more dilute ozone, but these substances are very explosive and have been but little studied.

Preparation. Oxygen containing 3–18 p.c. ozone is passed over a small quantity of the dry substance very slowly, the action being carried on for about 2 hours for every 3 grms. of ozonide formed. To moderate the reaction and to prevent explosion, the mixture and sometimes the ozone itself should be kept at a very low temperature; in the case of ethylene, however, the reaction proceeds quietly at 15°. For the same purpose, it is generally advisable to use an anhydrous solvent. The solvents formerly employed, hexane, carbon tetrachloride and chloroform, have been shown by Harries to be inconvenient as they are attacked by ozone. Benzene is dangerous, for it forms an explosive ozobenzene.

Glacial acetic acid would be a very good solvent, but most ozonides are too soluble in it and its boiling-point is too high for it to be readily distilled off or evaporated. Acetone is but slightly attacked. Ethyl and methyl chloride form very good solvents, but their cost prevents their more frequent use.

The ozonides are isolated by evaporating the solvent *in vacuô* below 20° and purified by solution in ethyl acetate and subsequent precipitation with light petroleum.

Properties. The ozonides are generally thick oils or colourless syrups with an unpleasant choking smell, and are mostly insoluble in light petroleum but soluble in most other organic solvents. They are generally explosive, but when they do not explode they may often be distilled *in vacuô* without decomposition; some, however, when thus treated, decompose into ozone and the original unsaturated substance. They have most of the properties of the peroxides, liberate iodine from potassium iodide and decolourise indigo and permanganate solutions. When reduced with aluminium amalgam they decompose thus:

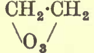


$$Me_2\underset{O-O-O}{C-CH}[CH_2]_2\cdot\underset{\underset{O=O}{\|}}{CMe}+4H$$
$$=Me_2CO+OCH[CH_2]_2COMe+2H_2O$$

or if the reaction is carried further, then with $10H=Me_2CH\cdot OH+OH[CH_2]_2CH(OH)Me+2H_2O$.

The ozonides of the higher aliphatic unsaturated hydrocarbons, containing one double bond and also those of the hydroaromatic hydrocarbons with one or two double bonds are, comparatively, very stable, but those of aliphatic hydrocarbons containing two double bonds are very readily decomposed. The 6- and 7-ring compounds seem to have similar stabilities towards boiling water, but the 5-ring compounds are much less stable than the two former classes. The ozonides of substances containing oxygen are very readily decomposed.

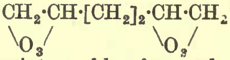
A large number of ozonides have been prepared of which the following may be described:

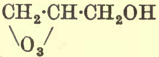
Ethylene ozonide  $\underset{\diagdown O_3 \diagup}{CH_2\cdot CH_2}$ is obtained by treating an absolutely dry solution of ethylene in methyl chloride with dry 7 p.c. ozone at about −70°, until the solution commences to be coloured blue. It forms a transparent colourless oil, b.p. 18°/16 mm., with a pungent odour, is readily volatile and explosive. If the ozone used is of higher concentration or the reaction is continued beyond the production of the blue colour, an *oxozonide* $C_2H_4O_4$ is formed (Harries and Koetschau, Ber. 1909, 42, 3305).

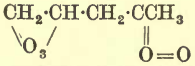
The ozonides and oxozonides of the homologues of ethylene are generally explosive, unstable substances, and have been obtained similarly, using ethyl chloride as solvent.

Ethyl alcohol, when treated with a stream of concentrated ozone, yields a peroxide, which has some of the properties but is not identical with ethyl hydroperoxide $C_2H_5O\cdot OH$.

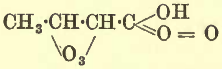
Aliphatic aldehydes, when treated with ozone, yield peroxides of the type RHC:O:O, which have not been obtained pure, owing to the readiness with which they are transformed into the isomeric acid.

Diallyl diozonide  $\underset{\diagdown O_3 \diagup}{CH_2\cdot CH}\cdot[CH_2]_2\cdot\underset{\diagdown O_3 \diagup}{CH\cdot CH_2}$ formed by passing ozone into a chloroform solution of diallyl, is a colourless syrup which, when heated, yields succinic dialdehyde and a little succinic acid.

Allylalcohol ozonide  $\underset{\diagdown O_3 \diagup}{CH_2\cdot CH}\cdot CH_2OH$ is a transparent syrup which decomposes at ordinary temperature.

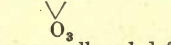
Allylacetone perozonide  $\underset{\diagdown O_3 \diagup}{CH_2\cdot CH}\cdot CH_2\cdot \underset{\underset{O=O}{\|}}{C}CH_3$ is a clear explosive syrup which decomposes on treatment with water forming formaldehyde, lævulic aldehyde and hydrogen peroxide.

*iso***Crotonic acid perozonide**

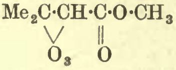


$$\underset{\diagdown O_3 \diagup}{CH_3\cdot CH\cdot CH}\cdot C\begin{matrix}\diagup OH\\ \diagdown O=O\end{matrix}$$

is a yellowish clear explosive syrup, which on standing, evolves oxygen and yields *iso*crotonic acid, whilst with water it yields acetaldehyde, glyoxylic acid and hydrogen peroxide.

Mesityloxideozonide  $\underset{\diagdown O_3 \diagup}{Me_2C\cdot CH}\cdot CO\cdot CH_3$ is obtained by treating 10 grms. well-cooled freshly distilled mesityl oxide with 12–14 p.c. ozone and a current of well-cooled carbon dioxide for about five hours, when a sample no longer decolourises an acetic acid solution of bromine. It is a thinner and less explosive oil than the perozonide, is miscible with all solvents except light petroleum and is readily decomposed by water and on heating.

When the mesityl oxide is saturated with ozone, *mesityloxideperozonide*



$$\underset{\diagdown O_3 \diagup}{Me_2C\cdot CH}\cdot\underset{\underset{O}{\|}}{C}\cdot O\cdot CH_3$$

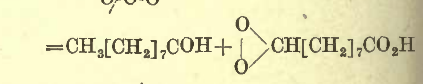
is formed as a thick green oil, highly explosive and spontaneously inflammable.

Methylheptenone yields similar normal and perozonides.

Phorone yields a monozonide and a diozonide—the latter being formed only very slowly when the treatment with strong ozone is very prolonged.

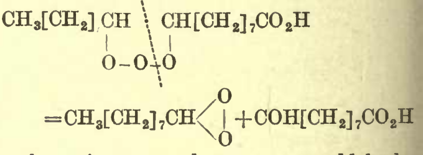
Oleic Acid Ozonides.

The *normal monozonide* $C_{18}H_{34}O_5$ is formed when oleic acid in acetic acid solution is treated with 0·5–18 p.c. ozone until a sample no longer decolourises a bromine solution of glacial acetic acid; or by washing the perozonide with water and sodium bicarbonate. It is a colourless, transparent, viscous liquid, heavier than water and when warmed with aqueous caustic soda yields a pleasant sharp smelling product, b.p. 90°. When treated with water it yields nonaldehyde, pelargonic acid, azelaic acid and an aldehyde product which, on oxidation, yields azelaic acid. The reaction is explained thus:

I. 

$$CH_3(CH_2)_7\underset{\underset{O}{|}}{CH}\,/\,\underset{\underset{O-O}{|}}{CH}[CH_2]_7CO_2H$$

$$=CH_3[CH_2]_7COH+\begin{matrix}O\diagdown\\ |\quad\ \\ O\diagup\end{matrix}CH[CH_2]_7CO_2H$$

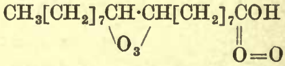
II. 

$$CH_3[CH_2]_7\underset{\underset{O-O}{|}}{CH}\ \diagdown\ \underset{\underset{O}{|}}{CH}[CH_2]_7CO_2H$$

$$=CH_3[CH_2]_7CH\begin{matrix}\diagup O\\ \quad |\\ \diagdown O\end{matrix}+COH[CH_2]_7CO_2H$$

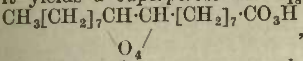
thus the primary products are nonaldehyde, nonaldehyde peroxide, azelaic acid half aldehyde (which is a decomposition product of almost all the ozonides of the higher aliphatic unsaturated acids), and the peroxide of the latter. By the isomerisation of the peroxides, pelargonic and azelaic acids are then formed. When warmed with glacial acetic acid the same products are obtained, but more peroxides are formed, whilst if formic acid is added to the acetic acid, considerably more aldehydes result. Similar products are also obtained by reducing the ozonide with sulphur dioxide or with aluminium amalgam in aqueous solution. Unstable ammonium, copper and sodium salts of oleic ozonide have been obtained.

Oleic acid perozonide



$$CH_3[CH_2]_7\underset{\diagdown O_3 \diagup}{CH\cdot CH}[CH_2]_7\underset{\underset{O=O}{\|}}{C}OH$$

is formed when a glacial acetic acid or carbon tetrachloride solution of oleic acid is treated with 10–12 p.c. ozone for an hour for each gram of acid. It is a somewhat thicker liquid than the ozonide but has similar chemical properties to the normal ozonide. When oleic acid is treated with 10 p.c. ozone for a very long time (3 hours per gram) or for a somewhat shorter time (4 hours for 5 grms.) with 16–18 p.c. ozone, it yields a *superperozonide* $C_{18}H_{34}O_7$, possibly



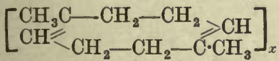
$CH_3[CH_2]_7CH\cdot CH\cdot[CH_2]_7\cdot CO_3H$ with O_4 bridging the two CH groups, which is a colourless substance, not much more explosive than the other ozonides and has the same general chemical properties.

Elaidic acid yields a normal and a perozonide which seems to differ little if at all from those of oleic acid.

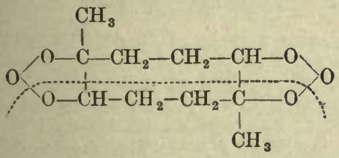
Citronellic acid yields a similar ozonide, per- and superperozonide (Harries and Himmelmann, Ber. 1908, 41, 2187).

Cholesterol ozonide $C_{27}H_{46}O_5$, which is probably an oxozone derivative, forms a very stable white powder and, when boiled with water, yields hydrogen peroxide, aldehydes and much resinous products. Similar ozonides of cholesterol derivatives have also been obtained (Diels, Ber. 1908, 41, 2596; Langheld, *ibid.* 1023).

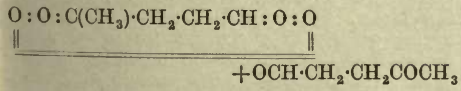
The most interesting application of the formation of ozonides to the elucidation of the structure of a compound is perhaps that of rubber. When the latter is treated with 5·5–6 p.c. of ozone, in chloroform solution for one hour for every gram, and the product evaporated *in vacuô* below 20° and the residue purified in the usual way, a *diozonide* $C_{10}H_{16}O_6$ is formed as a yellow thick oil. It dissolves in various solvents yielding, not colloidal, but ordinary solutions, and when boiled with water or distilled with steam it yields lævulic aldehyde and acid, and lævulic aldehyde superoxide. The formation of this ozonide and its decomposition products, together with the fact that when heated, rubber yields, amongst other products, *iso*prene and dipentene, has led Harries to give the following formula to rubber



which agrees very well with its other known reactions. With ozone, it would form the diozonide



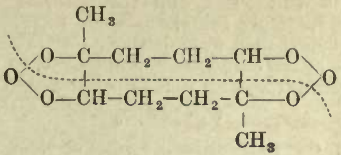
which, on decomposing, breaks at the dotted lines and therefore yields



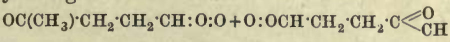
$$O:O:C(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O$$
$$+OCH\cdot CH_2\cdot CH_2COCH_3$$

Lævulic aldehyde diperoxide is readily transformed to the aldehyde in the presence of steam, consequently the lævulic aldehyde is present in large quantity (Harries, Ber. 1905, 38, 1195).

Gutta-percha gives a diozonide which seems identical with rubber diozonide, but on decomposition with water, it yields much less aldehyde and more acid: its decomposition has therefore been represented as taking place chiefly thus



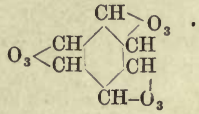
yielding



$$OC(CH_3)\cdot CH_2\cdot CH_2\cdot CH:O:O+O:OCH\cdot CH_2\cdot CH_2\cdot C{<}^{O}_{CH}$$

the latter readily being transformed into acid. The difference in behaviour of the two ozonides on decomposition is assumed to be due to some form of stereo-isomerism (*ibid.* 3985).

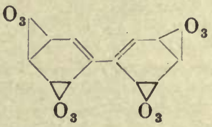
Benzene triozonide or **ozobenzene**



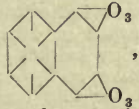
is formed by passing absolutely dry 5 p.c. ozone into dry benzene at 5°–10° for about 2 hours. It is stable in dry air at the ordinary temperature and forms a white amorphous mass which, if quite pure, becomes crystalline when treated with water at 0°. It is soluble in acetic acid but not in other organic solvents. When warmed quickly it explodes violently, and when treated with water it yields chiefly glyoxal OHC·CHO and some glyoxylic acid which probably results from the oxidation of the aldehyde with the hydrogen peroxide formed in the first reaction. These reactions show almost conclusively that benzene has three double linkings and that Kekulé's structural formula for benzene is correct.

Only the decomposition products of the triozonides of toluene *o*- and *m*-xylene and of mesitylene have been obtained.

Diphenyl forms a *tetraozonide*



obtained as a crystalline mass, which explodes violently when heated. The fact that two more ozone molecules are not added at the double linkings is probably due to steric hindrance.

Naphthalene, when strongly cooled and submitted to the action of ozone, yields a crystalline *diozonide*, thus  , indicating that, in all probability, only one of the rings has the benzene or Kekulé structure, whilst the other, possibly, has the concentric form. When treated with water the diozonide yields phthalic aldehyde $C_6H_4(CHO)_2$, phthalic acid, glyoxal, and glyoxylic acid.

Phenanthrene when treated similarly also forms a diozonide $C_{14}H_{10}O_6$ having similar properties to the naphthalene diozonide.

Tetrahydrobenzeneozonide $C_6H_{10}O_3$, obtained by passing ozone into a chloroform solution of the unsaturated hydrocarbon, forms elastic lumps, sparingly soluble in most solvents, and when boiled with water yields *n*-adipic acid and a little of the corresponding aldehyde.

m-**Dihydroxylene** yields a diozonide

$$C_6H_6Me_2O_6$$

which, on purification, forms a clear syrup with a characteristic smell. It is comparatively stable, but sometimes explodes with great violence (Harries and Neresheimer, Ber. 1906, 39, 2846).

Literature. Harries, Annalen, 1905, 343, 311; *ibid.* 1910, 374, 288; Ber. 1912, 45, 809; Lebédeff, J. Russ. Phys. Chem. Soc. 1910, 42, 949; Drugman, Chem. Soc. Trans. 1906, 939; Dyckerhoff, Antoxydation organischer Stoffe, Inaug. Dissert. Karlsruhe, 1910; Valeur, Action de l'Ozone sur les composé Organique, Paris, 1909.

P

PACHNOLITE (πάχνη, rime). A fluoride of aluminium, calcium, and sodium, occurring as an incrustation or efflorescence on cryolite. It is regarded by Knop as a hydrated cryolite in which two-thirds of the sodium are replaced by calcium (A. Knop, Annalen, 127, 61).

Composition.—

Al.	Ca.	Na.	F.	H_2O.
13·43	17·84	10·75	49·78	8·20 = 100·00

PACKFONG or **PACKTONG.** A Chinese alloy resembling nickel silver, and of a similar composition.

PACO or **PACOS.** A Peruvian term for a ferruginous earth or ore containing small quantities of metallic silver.

PÆONINE (*Red Coralline* or *Aurine R.*) *v.* AURINE.

PAINT OILS. Under this term are comprised those vegetable oils which are used as vehicles for applying pigments to the surface of bodies, either as a preservative or for decorative purposes. Only the vegetable drying oils are useful; the paint oil, *par excellence*, is linseed oil. The semi-drying oils, such as cotton seed oil and maize oil, are unsuitable as paint oils. Nor is soya bean oil suitable as a paint oil, although when the price of linseed oil was high it was largely used as a substitute for linseed oil or to adulterate linseed oil. Fish oils, which are used as adulterants to an enormous extent, are unsuitable as paint oils, notwithstanding frequently made statements to the contrary. Adulteration with rosin oil is practised on an extensive scale, although more easily recognised than adulteration with animal and vegetable oils of somewhat lower iodine value than linseed oil. Oil extracted by solvents is not suitable as a paint oil. J. L.

PAINTS. *Definition.*—Coloured mixtures, usually liquids, with which suitable surfaces can be coated by a brush or other means. The coverings formed may be dull or lustrous, and often act as protectives and preservatives of the surfaces beneath. Usually, paints differ from varnishes in yielding coatings possessing less lustre, and in the absence of resinous ingredients: but enamel paints and various special products are of exceptional composition. Ordinary paints consist essentially of three parts, the *pigment*, the *medium* or vehicle, and the *drier* or siccative. Paints manufactured for particular uses, such as luminous paints, anti-corrosive paints, and waterproof paints, contain other components of the most diverse kinds.

Surfaces only are covered by paints :, dyes stain throughout. This distinction is maintained in the present article, from which is excluded the consideration of dyes. The term 'pigment' will be confined to those substances to which paints owe their colours; mostly dry powders, finely diffusible but insoluble in the binding and thinning media employed. 'Paint' will be employed in reference to the combination of pigment and medium, ready for use by the painter. Pigments will first be described, and then the vehicles by which these pigments are converted into paints. Driers come next in order: lastly, paints themselves.

Pigments. *Definition.*—Finely divided insoluble coloured powders, yielding paints when intimately mixed with suitable media.

Origin.—Pigments are obtained from mineral, vegetable, and animal sources, chiefly the first-named. Inorganic pigments comprise minerals and manufactured products, mostly metallic salts or oxides: such pigments are usually more permanent than those of vegetable or animal origin.

Characters.—1. Body or opacity, *i.e.* the property of completely covering and concealing the surface beneath. 2. Covering or spreading power; the extent to which a pigment can be spread over a large surface. 3. Drying quality, when combined with a medium to form paint. 4. Durability or permanency. 5. Tint. 6. Shade.

Pigments may be of all degrees of opacity, and they also differ greatly in density and in the state of aggregation of their particles. Some are opaque and amorphous; others are crystalline and translucent or transparent. The higher the density and opacity of a pigment, the greater is its body. Crystalline powders, however impalpable, have less opacity than amorphous powders, hence the superiority of the latter, as regards covering power. The drying quality of a pigment (in an oil paint) depends upon its power of oxidising or promoting the oxidation of the medium with which it is mixed: this property is possessed in a much greater degree by some pigments than by others and siccatives must be added when the pigment is known to be deficient in this characteristic. Permanency is tested by the power of the pigment, when made into paint, of resisting the action of light, moisture, fetid gases, acid and alkaline vapours, exposure to the atmosphere, &c. In special circumstances, as for the colouring of a lime-plastered surface, for fresco work, or the like, pigments must be unaffected by, or 'fast' to, lime. As a rule, pigments are more durable when mixed with oil than when used in aqueous media. Instances are known of pigments in admixture exercising a detrimental influence upon one another. In oil media, this action is rarer than has been supposed: but an example is the darkening of the green pigment made by mixing cadmium yellow with emerald green, the last-named being, to a slight extent, dissolved by the linseed oil and therefore enabled to react upon the cadmium sulphide. Tint depends upon chemical composition, molecular constitution, physical condition, and the mode of production. The exact shade is a resultant of many niceties of detail during the processes in the colour factory. In a case, for example, where the pigment has been precipitated from solution, the shade will vary with the amount of care devoted to the washing of the precipitate—a very small percentage of impurity being the cause of a marked difference in quality. The degree of subdivision of a pigment also has a most important influence on the shade. Of great weight are the extent of dilution of the solutions, and the amount of efficient agitation, or mixing. The precipitated pigments are usually finer and brighter in shade, in direct proportion to the dilution of the solutions employed.

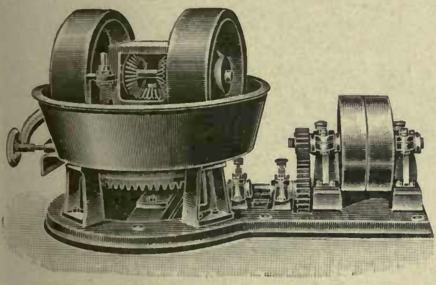


FIG. 1.

Positive Driven Edge Runner Mill (Brinjes and Goodwin, Ltd.).

Preparation.—The pigments of commerce are so numerous that it will be impossible to describe the manufacturing processes by which most of them are obtained; but the important operation of grinding must be mentioned. All pigments must be in an extremely fine state of division. The colours used by house-painters and paper-stainers are pulverised and mixed by paint-grinders, while the more numerous and brilliant pigments used in the fine arts are ground by artists' colourmen. Formerly, most pigments were ground by hand on a grinding stone with the aid of a muller, but the unhealthy and dangerous nature of the operation, especially when orpiment, white and red leads, chrome yellow, and many other important pigments, were treated, led to the introduction of colour mills, in which larger quantities of pigments can be ground and mixed in covered vessels, so that the risk to the workmen is very greatly lessened.

Colour grinding.—On the larger working scale, pigments are *dry-ground* chiefly in under-driven edge-runner mills: on a somewhat smaller scale, conoidal mills, which are especially serviceable for materials composed of soft fragments, may be used. The centrifugal mills known as 'disintegrators' are exceedingly convenient. Fig. 1 shows one of the positive-driven edge-runner mills, manufactured by Brinjes and Goodwin, Ltd., of Whitechapel. In this machine, the movement around the pan, and the revolution of each stone upon its axis, are caused by special gearing. Other types of edge-runner mills, top-driven, are represented in Fig. 2 (same makers) and Fig. 3 (Bryan Corcoran, Ltd., London). The fourth illustration shows an under-driven mill of a similar description

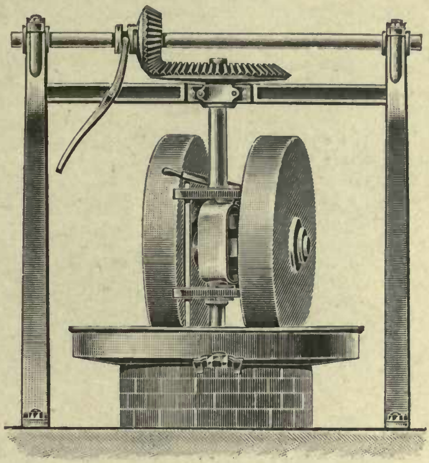


FIG. 2.

Edge Runner Mill, over Driven (Brinjes and Goodwin, Ltd.).

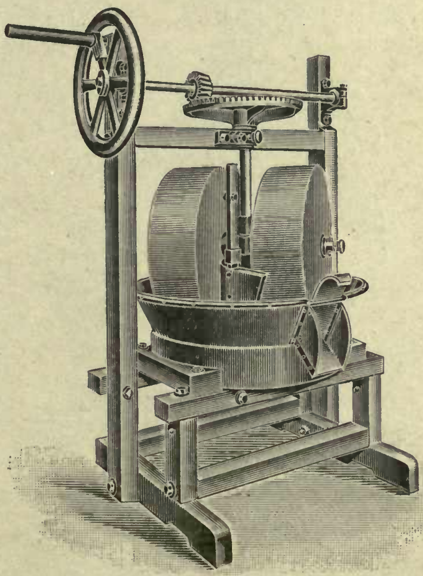


FIG. 3.

Edge Runner Mill, Top Driven (Bryan Corcoran, Ltd.).

(Wm. Gardner & Sons, Ltd., Gloucester). The bottom-driven type of mill is for colour-grinding preferable to, and now more generally used than, the top-driven kind. The bed and runners of these mills for colour-making should be of granite. When large fragments of highly resisting materials have to be dealt with, a less rigid form of mill than the positive-geared is to be recommended.

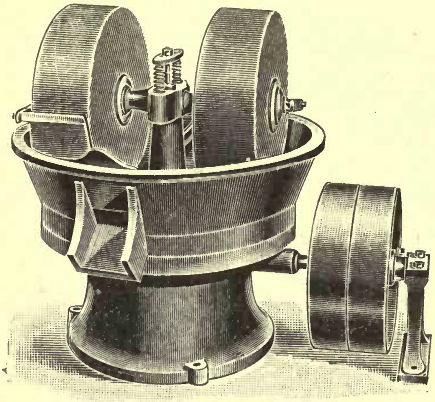


Fig. 4.

Underdriven Edge Runner Mill (Wm. Gardner & Sons, Ltd., Gloucester).

A conoidal mill, supplied by Bryan Corcoran, Ltd., of Mark Lane and Whitechapel, is shown in Fig. 5, and in Fig. 6 is represented a disintegrator (Wm. Gardner and Sons, Ltd., Gloucester).

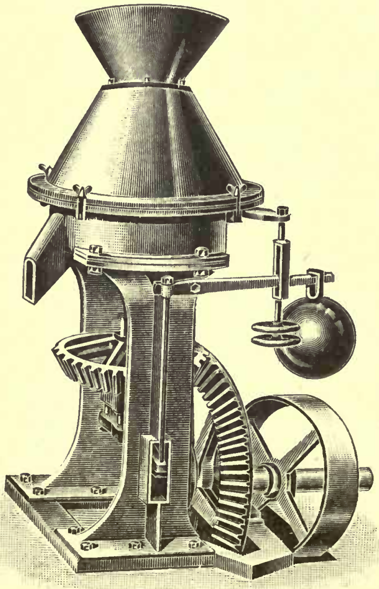


Fig. 5.

Conoidal Mill (Bryan Corcoran, Ltd.).

Pigments may be *wet-ground* in a levigating edge-runner; in a pulveriser of special construction, such as the 'Alsing' pulveriser; or, if the required output be small, in a levigating flat-stone mill. Edge-runner mills are mostly used.

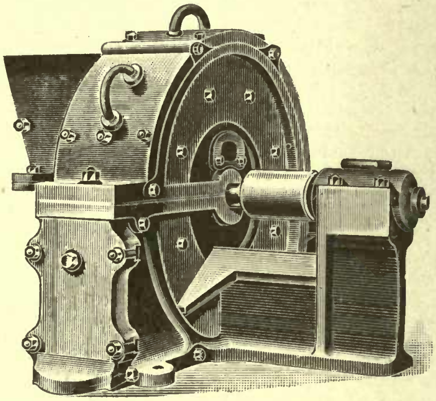


Fig. 6.

A Disintegrator (Wm. Gardner & Sons, Ltd.).

Paint grinding.—The older type of machine for the *grinding of mixed paints* was the ordinary flat-stone mill (Fig. 7), but the triple roller grinding mill (Fig. 8) has almost entirely superseded it.

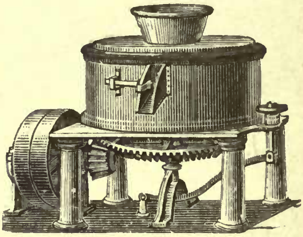


Fig. 7.

Flat Stone Mill (Brinjes and Goodwin, Ltd.).

Paint mixing, which precedes the grinding, is usually conducted either in a vertical mixer similar to that shown in Fig. 9, or in a horizontal mixer, which may be of the kind depicted in Fig. 10. In certain cases, however, as in the mixing of zinc paint, a positive-geared edge-runner mill (Fig. 1) is the best to use. If a

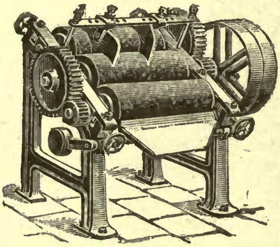


Fig. 8.

Triple Roller Grinding Mill (Brinjes and Goodwin, Ltd.).

volatile medium be necessary, as in the production of enamels, a conoidal mill (Fig. 5) may conveniently be substituted.

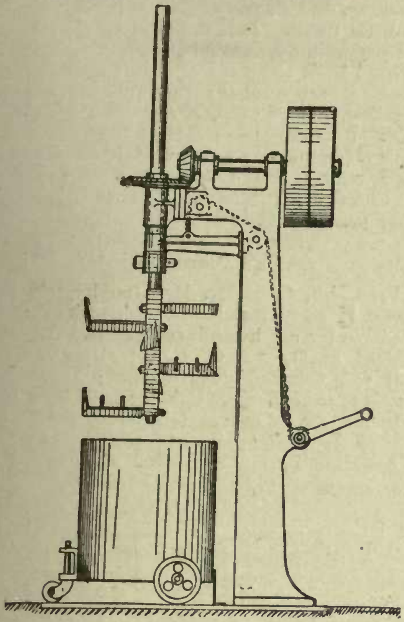


FIG. 9.

Ready-mixed Paint Mixer, with Double-acting Stirrers (Brinjes and Goodwin, Ltd.).

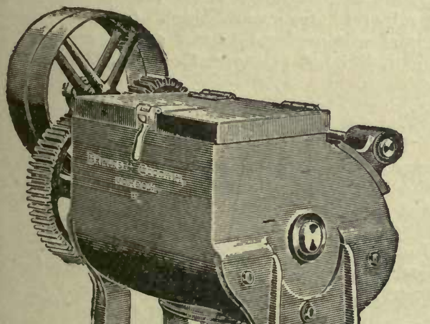


FIG. 10.

Geared Horizontal Mixer (Brinjes and Goodwin, Ltd.).

The more important and widely used pigments, classified according to colour, will next be briefly described. For further details *v.* art. PIGMENTS.

WHITE PIGMENTS.

White Lead (*Céruse, Cerussa Alba, Blanc de Plomb, Krems white, Bleiweiss*). For manufacture *v. White lead*, art. LEAD.

Characters of good white lead.—A perfectly amorphous white pigment, possessing great opacity, density, and covering power, and the property of drying rapidly when mixed with linseed or a similar oil, and exposed to the air. The hydroxide combines with the oil, forming a white elastic coating or paint; but lead hydroxide alone would give little opacity, which is imparted by the carbonate present. The latter forms an emulsion with the oil, of extreme opacity. Both, then, are essential.

Additions to, and diluents of, white lead.—Barium sulphate and chalk principally; but calcium sulphate, clay, lead sulphate, &c., are also added. Most of the cheaper so-called white lead in the market contains an admixture of barium sulphate or some other comparatively inexpensive white pigment. Certain of these substances are themselves used as white pigments of inferior quality.

Substitutes for white lead.—The chief, if not the only, objections to white lead as a pigment are its poisonous character and its tendency to darken in an atmosphere containing sulphuretted hydrogen. Many substances are used as substitutes, but all are inferior to white lead in body. Sulphate of lead (*Mühlhausen white*); oxychloride of lead (*Pattinson's white*); a mixture of lead sulphate, barium sulphate, zinc white, and magnesium carbonate (*Freeman's non-poisonous white lead*); '*sublimed white lead*' (lead sulphate 75 parts, lead oxide 25 parts, and zinc oxide 5 parts); '*standard zinc lead white*' (lead sulphate 50 p.c., zinc sulphate 0·40 p.c., zinc oxide 49·55 p.c.); zinc oxide; zinc sulphide; and a mixture of oxide, sulphide, and sulphate of zinc, have been manufactured for this purpose. A calcined mixture of 70·5 p.c. of barium sulphate with 29·5 p.c. of zinc sulphide, prepared by precipitating a solution of barium sulphide with a solution of zinc sulphate, washing, pressing, drying and 'firing' the resulting precipitate, constitutes the pigment known as *Lithopone, Orr's white, Charlton white*, or *Beckton white.* One of the most useful and valuable substitutes for white lead, lithopone, is quite unaffected by sulphuretted hydrogen, is possessed of considerable body, permanency, and fineness of tint. It is far less injurious to health than white lead and yields an excellent oil-paint. *Sulfopone* is a similar pigment prepared from zinc sulphate and calcium sulphide. The addition of calcium sulphate is stated to counteract the discolouring effect of light and air upon lithopone. Among other white lead substitutes may be mentioned basic lead sulphite; oxide and silicate of zinc; zinc oxide with sulphide or chloro-sulphite of lead; mixtures of barium sulphate and calcium sulphate with zinc oxide, and basic chloride of zinc.

Other white pigments. The white pigments of commerce are known by a great variety of names. *Flake white, Berlin white, silver white*, and *Krems white* are names applied to very fine and pure varieties of white lead. *Venice, Hamburg* and *Dutch whites* are mixtures of white lead and barium sulphate in different proportions. *Blanc fixe*, *Baryta white*, *fast white*, and *Permanent white* are barium sulphate. *Strontium* or *Strontian white* is sulphate of strontium. Magnesia (MgO) and magnesium carbonate ($MgCO_3$) constitute *Magnesia whites*. *Spanish white* or *Paris white*, is *whitening*, or *whiting* ($CaCO_3$). Whitening, gypsum, kaolin, French chalk, asbestine, infusorial earth, &c., are used in mixed paints as 'extenders' or 'fillers,' and some of them, with lime, are employed as painting grounds, rather than as pigments. *Zinc white* and *Chinese white* are names given to zinc oxide. First employed on a commercial scale by Leclaire, c. 1847, this beautiful pigment is increasing in favour as a constituent of ordinary paints, and for the production of enamels, white oil-cloths, and the like. Zinc white possesses very fair covering power, though less than flake white: it is not visibly affected by sulphuretted hydrogen. It can be used with oil- or water-media—especially well with the last-named, and is non-poisonous. In an oil vehicle it dries far less rapidly than lead white. Admixture with calcium sulphate is alleged greatly to enhance the spreading power of zinc oxide. Carbonate of zinc has been employed as a pigment, but not very successfully. *Pearl white* is basic nitrate of bismuth [$Bi(NO_3)_3 \cdot 2Bi(OH)_3$], but the name is also used in connection with a lead white, tinted with indigo or some other blue pigment. Yet another *Pearl white* is bismuth oxychloride [$2(BiCl_3 \cdot Bi_2O_3) \cdot H_2O$]; and basic nitrate of bismuth is occasionally called *Flake white*. Whites of tin, cadmium, mercury, arsenic, tungsten, and antimony have all been tried, but without permanent success. Antimony white, however, is said to have considerable covering power. The oxide, Sb_4O_6, and powder of algaroth, $Sb_4O_6 \cdot 2SbCl_3$, are both used, but these pigments deteriorate on exposure.

YELLOW PIGMENTS.

Yellow ochres, *Terra di Siena*, *Stone yellow*, *Roman yellow*, *Mineral yellow*, *Oxford ochre*, *Golden ochre*, &c. Argillaceous earths, containing varying percentages of hydrated ferric oxide (very durable and trustworthy pigments). *Mars yellow* is an artificial preparation of similar composition. A pigment called by the same name, also termed *Siderin yellow*, is $Fe_2(CrO_4)_3$. *Chrome yellow* is $PbCrO_4$: also $PbCrO_4 \cdot PbSO_4$; and $PbCrO_4 \cdot 2PbSO_4$. Pale and greenish shades contain citrate or tartrate of lead, and sometimes also sulphate, as well as lead chromate. *Orange chrome yellow* is $PbCrO_4.PbO$. *Cologne yellow* is $PbCrO_4$, $PbSO_4$, and $CaSO_4$. (These yellows possess considerable body, but are affected by sulphuretted hydrogen.) *Strontium*, *Barium*, and *Zinc yellows*, $SrCrO_4$, $BaCrO_4$, and $3(ZnCrO_4)K_2Cr_2O_7$ (durable, but have little body). Barium chromate (*Lemon yellow*, *Yellow ultramarine*) is the most permanent of these pigments. *Bismuth yellow*, also a chromate (not permanent). *Cadmium yellow*, CdS, durable, of fairly good body, and unaffected by sulphuretted hydrogen. True *Naples yellow*, PbO,Sb_2O_5 (permanent in oil). Cadmium sulphide, and a pale yellow ochre, have been sold under the same name. *Montpellier*, *Cassel* ($PbCl_2.7PbO$), *Turner's*, *Turin*, *Verona*, and *Paris yellows*, oxychlorides of lead (not lasting). *King's yellow* or *Orpiment*, As_2S_3 (unstable). *Wolfram*, *Vanadium*, *Uranium*, *Thallium*, *Palladium*, *Tin*, *Antimony*, and *Platinum yellows* (most unstable and little used). *Indian yellow* or *Purree*, impure magnesium euxanthate, $C_{19}H_{16}MgO_{11},5H_2O$, prepared from the urine of cows fed on mango-leaves. A beautiful but variable pigment. *Madder yellow*, *Italian pink*, *Brown pink*, &c. (vegetable: non-durable—bleached on exposure). *Gamboge* (a vegetable resin; unstable). *Aureolin*, occasionally called *Cobalt* or *Indian yellow*, potassium cobaltinitrite, $K_6Co_2(NO_2)_{12},xH_2O$ (fairly permanent).

RED PIGMENTS.

Vermilion, *Cinnabar*, HgS (moderately permanent in oil: alterable in water-colour): too expensive for use in ordinary paints. *Minium*, *Red lead*, Pb_3O_4 or $PbO.Pb_3O_4$ (not permanent), *Light red*, calcined yellow ochre; *Indian red*, *Venetian red*, *Rouge*, *Colcothar*, *Bole*, *Caput mortuum*, &c.: ochres (all durable colours). Some of these pigments are artificially obtained by calcining ferrous sulphate. *Chrome red* or *Austrian cinnabar*, basic lead chromate,

$$PbCrO_4.PbH_2O_2,$$

and *Chrome oranges*, mixtures of normal and basic lead chromates (all unstable). *Realgar*, As_2S_2, arsenic sulphide. *Antimony vermilion*, antimonyoxysulphide, $Sb_6S_6O_3$. *Palladium red*, ammonio-chloride of palladium, and *Brilliant scarlet*, mercuric iodide (very unstable), have been used. *Vandyke red* is copper ferrocyanide, $Cu_2Fe(CN)_6$. The cobalt reds are too costly for general use. *Madder* lakes (vegetable colours on mineral bases; unreliable). *Carmine lake* (of animal origin—from *Coccus cacti*; a beautiful colour, but not permanent).

GREEN PIGMENTS.

Terre verte, an impure ferric silicate (permanent, but deficient in body when used as an oil-colour). Many salts of copper have been used as green pigments. Among the best known of the copper greens are *Malachite*, *Mountain green*, or *Green verditer*, hydroxycarbonate of copper, $CuCO_3,CuH_2O_2$, *Schweinfurt* or *Emerald green* (acetoarsenite),

$$3(CuAs_2O_4) \cdot Cu(C_2H_3O_2)_2,$$

Brunswick green (oxychloride), $CuCl_2 \cdot 3CuO,4H_2O$, and *Verdigris* (basic acetate),

$$2Cu(C_2H_3O_2)_2,CuO,6H_2O.$$

Scheele's green is a basic arsenite of copper, now but little used. *Mitis*, *Vienna*, and *Kirchberger greens* have the same composition. *Bremen green*, *Green ashes*, *Elsner green*, *Gentele's green* (stannate), and *Mineral green*, are other copper pigments. All are darkened by sulphuretted hydrogen, and most are very poisonous.

Mixed greens: *Brunswick green* (another kind), *German green*, *Hooker's*, *Leaf-*, *Milory-*, and *Silk-greens* are mixtures of various yellow and blue pigments, and can be dismissed as of very questionable value.

Chromium, *Guignet's*, *Pannetier's*, *Arnaudon's*, *Plessy's*, and *Chrome emerald greens* are hydrated sesquioxides of chromium, with phosphate or borate of chromium. *Viridian* is $Cr_2O_3,2H_2O$. All are permanent and full-bodied pigments (*v.* CHROMIUM). Other chromium greens are Casali's, Dingler's, and Schnitzer's products. *Rinmann's green, Cobalt green,* or *Zinc green,* a compound of oxide of cobalt and oxide of zinc. *Titanium, Vanadium, Uranium, Manganese, and Molybdenum greens* are also occasionally met with as pigments. *Green ultramarine* is a calcination-product in the manufacture of artificial ultramarine. There are many unstable green lakes of vegetable origin, such as *Chinese green, Iris green,* and *Sap green,* but they are of little or no value. Some of the green lake pigments prepared from the coal tar colours, however, possess considerable covering power and a measure of fastness to light.

Blue Pigments.

Prussian blue, Berlin blue, Chinese blue, &c., $Fe_7(CN)_{18}$ (liable to change). *Soluble Prussian blue,* of inferior quality to the preceding, is $K_2Fe(CN)_{12}Fe_2$. Antwerp blue is a light-tinted variety of Prussian blue. *Indigo,* or *Indigotin,* $C_{16}H_{10}N_2O_2$ (vegetable; fades on exposure). *Native ultramarine,* pulverised lapis lazuli (an excellent and stable, but costly colour). *Artificial ultramarine,* probably $Na_4(NaS_3Al)Al_2(SiO_4)_3$ (Brögger and Backström) a compound of silicate of aluminium and sodium, with sulphide of sodium; suggested by Gmelin, in 1827, and made by Guimet in 1828. Less expensive than native ultramarine, and nearly equal to it as a pigment. Both pigments are permanent in the absence of acids (*v.* ULTRAMARINE). *Thénard's blue,* phosphate and aluminate of cobalt. *Cobalt blue, Gahn's ultramarine,* aluminate of cobalt. *Cyanine, Leitch's blue,* a mixture of cobalt blue and Prussian blue. *Smalt, Zaffre, Royal,* and *Saxony blues,* glasses coloured by cobalt oxide. *Cœruleum,* $3(SnO_2\cdot CoO)+SnO_2$ (stannate of cobalt). The cobalt colours lack somewhat in body and permanency. *Copper blues,* carbonates, silicates, and other salts of copper, are of little value.

Brown Pigments.

Vandyke, Rubens, Cassel, Ulmin, and *Cologne browns*: some of these are partly vegetable, and are prepared from peat, cotton, soot, &c.; bituminous matter is often present. Several different pigments are known as *Vandyke brown.* Only those prepared by calcining highly ferruginous brown ochres, or consisting of a dark-tinted form of colcothar, are permanent. The variety of Vandyke brown, consisting of a bituminous earth, is far less durable. *Burnt sienna, Brown terre verte, Raw* and *burnt umber, Cappagh brown,* and *Mars brown,* are earths or ochres, raw or calcined. Most of them are durable and reliable pigments. Other browns are *Prussian brown,* made by calcining Prussian blue; *Madder brown* (of vegetable origin, and liable to fade); *Bistre,* a bituminous brown; *Asphaltum*; and *Mummy.* The last three also are untrustworthy and fugitive.

Black Pigments.

Ivory black, Bone black, Lamp black. These are more or less pure carbon, and the names are self-explanatory. *Indian ink* consists of very fine lamp black, together with gelatin and a perfume (*v.* INDIAN INK). *Blue-black, Frankfort black,* or *Drop black* is made from vine twigs, ivory cuttings, bone shavings, peach stones, and other organic materials, which are calcined until complete charring is effected. After grinding, the black so obtained is made up with glue and water into pear-shaped drops for sale. *Manganese black* is native peroxide of manganese. All these black pigments are very durable. *Sepia* is a brownish-black pigment derived from the ink-bag of *Sepia officinalis*: it is alterable by sunlight, but less so than *Vandyke brown,* &c.

Of the above-mentioned pigments, only a few (chiefly the ochres, lamp-black, red lead, white lead, zinc white, baryta white, Prussian blue, chrome yellow, orange and red, vermilion, and the commoner copper greens) enter into the constitution of the paints used by decorators and house-painters; white lead is nearly always the base, and is largely in excess of the other pigments present, which are technically called the '*stainers.*' The finer varieties of these colours and many of the other pigments, are used habitually or occasionally by artists. Of pigments not named in this article, there are many which are simply fancy preparations, with no good qualities to recommend them.

As regards durability, it may shortly be stated that all the compounds of copper, lead, and bismuth, and some mercurial pigments, darken more or less, when exposed to air containing sulphuretted hydrogen. Most of the colours which are partly or entirely of organic origin fade on exposure, by a process of oxidation. On the other hand, pigments which are not affected by foul gases, the barium and zinc whites, for example, have unfortunately, for the most part, less covering power than the majority of lead, copper, and other changeable pigments. Great circumspection must, therefore, be exercised in the choice of a pigment, whether for artistic or ordinary work. As a rule, pigments are less fugitive in oil-media than when mixed with the usual water-colour vehicles. Church (The Chemistry of Paints and Painting, 1901) classifies artists' pigments, according to their stability in oils, as shown in the table, page 74.

To adapt this table to water colours, the pigments marked × must be relegated to class III.: while Indian ink, bistre, and sepia may be added to the table. But the two last named must be placed in class III.

The following examples of carefully chosen palettes are quoted from Church's work, just cited: (*a*) for *oil-painting,* flake white, yellow ochre, cadmium yellow, aureolin, vermilion, madder carmine, ultramarine, viridian, Cappagh brown, and ivory black: (*b*) for *water-colours,* Chinese white, yellow ochre, cadmium yellow, aureolin, red ochre, madder carmine, ultramarine, viridian, Mars brown, and Indian ink.

Media or Vehicles. *Definition.*—The fluids or other materials with which pigments are intimately mixed for the production of paints. For *oil-paints,* the vegetable drying or siccative oils are employed, and for *water-colour paints,* size, honey, glycerol, and aqueous solutions of gums, or the like, are in use. Oil of turpentine is frequently added to the oil medium, acting partly as a 'thinning' agent, and partly to accelerate somewhat the drying of the paint. Benzene,

Class I. Truly permanent.	Class II. Somewhat changeable.	Class III. Untrustworthy.
Baryta white.	Aureolin.	King's yellow.
Zinc ,,	Baryta yellow.	Yellow madder.
×Flake ,,	Indian ,,	Brown pink; yellow lake.
Yellow ochre.	Strontia ,,	Gamboge.
Raw sienna.	×Chrome ,,	Zinc chromate.
×Naples yellow, true.	Madder carmine.	Crimson lake.
×Cadmium ,,	Rubens' madder.	Carmine and burnt carmine.
Cadmium orange.	Rose ,,	Indian lake.
×Vermilion, artificial.	Madder red.	Scarlet ,,
Vermilion, native.	Purple madder.	Purple ,,
Indian red.	Mars violet.	Violet carmine.
Light ,,	Emerald green (Schweinfurt g.)	Verdigris.
Venetian red.	Terre verte.	Sap green.
Red ochre.	×Malachite.	Green vermilion, etc.
Cobalt violet.	Smalt.	Indigo.
Manganese violet.	Prussian blue.	Blue verditer.
Viridian (emerald oxide of chromium, $Cr_2O_3,2H_2O$).	Antwerp ,,	Blue ochre.
Green oxide of chromium, Cr_2O_3.	×Madder brown.	Bituminous Vandyke brown.
Cobalt green.	Cologne earth.	
Green Ultramarine.	Bitumen.	
Ultramarine.	Earthy Vandyke brown.	
Artificial ultramarine.		
Cobalt.		
Cœruleum.		
Burnt sienna.		
Raw and burnt umber.		
Cappagh brown.		
Verona ,,		
Prussian ,,		
Ivory black.		
Charcoal black.		
Lamp-black.		
Graphite.		

and turpentine substitutes, allied to petroleum spirit, are similarly used. In *tempera-painting* albuminous or gelatinous media are employed, and water-glass is the vehicle in *stereochromy.* Lime-water or baryta-water is used in *buon, fresco,* and *fresco-secco* painting. In *pastel painting,* the bases for the pigments are whitening, and (sometimes) plaster of Paris, or kaolin. Beeswax was the medium in Greek and Egyptian *encaustic* work, and is employed in *spirit-fresco.* Other paint-media are occasionally made use of, and will be referred to presently.

Oils. These are chosen for their drying properties, or, in other words, their power of absorbing oxygen when spread in thin layers and exposed to the atmosphere; by this oxidation a film of a drying oil gradually becomes converted into a coherent coating of a hard, elastic, varnish-like substance.

Linseed oil is the most important and commonly used drying oil; it is met with in commerce under the names of *raw, refined, artists',* and *boiled* oil. Raw oil is as expressed from the seeds. By agitation in lead-lined tanks with 1 p.c. of strong sulphuric acid, boiling with water or treatment with steam, and drawing off in settling-tanks from water and sediment, raw oil is converted into refined oil. Artists' linseed oil has been allowed to stand for weeks or months, then treated with litharge and finally bleached by exposure. Other processes of refining are also used. Boiled oil has been heated in air to 130°, or thereabouts, and maintained at that temperature for a little while. Raw linseed oil possesses great drying powers, which are considerably enhanced by the operation of boiling. Boiled oil is therefore a most important article to the painter. The drying power of boiled oil is still greater if litharge or some other drier has been added during the operation of boiling. The drier appears to act as a carrier of oxygen to the oil, and a definite chemical compound of the metallic oxide with linoleic acid is at the same time formed (*v.* OILS, FIXED, AND FATS; DRIERS). Both raw and boiled linseed oil are used in the manufacture of ordinary paints, while for the more delicate colours employed in the fine arts, refined and artists' oil are preferred.

Poppy, walnut, hempseed, and castor oils are also used in the manufacture of paints, particularly poppy, walnut, and hemp oils. These oils are, however, almost exclusively used by artists; and linseed oil holds its own as the most generally useful and applicable drying oil. Numerous additions to, and substitutes for linseed oil have been tried, among them mineral and resin oils, China wood oil (Tung oil), Niger-seed oil, cottonseed oil, and menhaden oil.

Artists in oil generally use media which contain copal, amber, or some other resinous varnish, and a diluent, such as turpentine, in addition to the drying oil. A good artists' medium can be prepared by gently warming a mixture of linseed or poppy oil with strong copal varnish and a trace of bleached beeswax. A less satisfactory medium is 'megilp,' composed of linseed oil and mastic varnish. Such media are added to the mixed colours by the artist.

The vehicles for water-colour paints need no description; they are, chiefly, isinglass, size, gum-water (gum-arabic, gum-tragacanth, and gum-senegal are all used), honey, dextrin, and glycerol. Of the gums, gum-senegal is the most suitable. Dextrin is less adhesive and less brittle than gum. An alcoholic solution of honey-lævulose is preferable to honey itself.

The various 'pastes,' 'fritts,' and 'glazes,' used for ceramic ware, enamels, painted glass, and the like, are outside the scope of this article (*v.* FRITTS AND GLAZES; POTTERY).

Driers or **Siccatives.** The effect of these on the drying oils has been referred to. The driers mostly employed are litharge, acetate of lead, resinates of manganese and lead, manganese dioxide, and manganous borate. Manganese oxalate, manganese linoleate, calcium borate, zinc borate, zinc oxide, zinc sulphate, burnt alum, lime, red lead, and ferric oxide are sometimes used. 'Terebines' or 'liquid driers' are solutions of certain of the above-named metallic organic compounds in linseed oil and turpentine. White lead itself has considerable siccative power; this is one reason why it is so especially useful a pigment. The 'driers' of house-painters are commonly sold ready ground up with boiled oil. They must be used with care, as they sometimes detract from the delicacy of the colour with which they are mixed; and for this reason the use of driers should be avoided as much as possible in paints intended for 'finishing coats.'

Paints. The mixed colours, ready for use. Common oil-paints consist of the pigments (generally white, lead or a substitute, such as lithopone, together with small proportions of the desired 'stainers'), ground with oil in the paint mill to a thick paste, and mixed with 'driers.' They are sometimes manufactured and supplied as 'ready-mixed' paints (in which the painting of comparatively small articles can be effected by the simple operations of dipping and subsequent draining), but usually require 'thinning down' with oil of turpentine to the required consistency. The oil for outdoor work is usually boiled oil; while for indoor painting pale linseed oil is frequently used, together with a larger proportion of driers. The smaller the quantity of oil used, the greater is the ultimate hardness and the less the lustre of the paint. Distemper painting, for absorbent surfaces, such as plaster, necessitates the application of a 'priming,' consisting of white lead, or, very commonly, whiting, ground in water and mixed with size. There is little to specify in reference to artists' oil-paints, excepting that they consist, or should consist, of *pure* pigments very finely ground in, and intimately mixed with, oil of the best quality, no base, such as white lead, being present. The proportion of oil used varies with the pigment, and ranges from less than 20 parts per 100 of pigment, for materials such as lead and zinc whites, to over 175 parts per 100 for colours such as raw sienna, burnt sienna, and the like. Artists' water-colour paints are met with in the forms of cakes, pastilles, and tube-colours. Cakes and pastille colours are usually made by grinding the pigments into a paste with a mixture of isinglass, size, and gum-water; the paste is then compressed and dried at a moderate temperature. Such paints are ground on the palette with water before use. Tube or moist colours consist of the pigments made into a cream with honey, glycerol, &c. Glycerol is preferable to honey.

Many other kinds of paints besides those already mentioned are manufactured at the present time. The principal of these are the luminous, fireproof, damp-resisting, anti-corrosive, water, washable, and enamel paints; their composition is very varied, and only a few short notes can be included in reference to them.

Luminous paints contain phosphorescent sulphur-compounds of strontium, barium, or calcium, sometimes associated with bismuth, uranium, and other salts. The mixtures are submitted to a calcination process, and combined with suitable pigments and media. Balmain's, Vanino's, Mourel's, and Lennord's luminous paints are well-known preparations belonging to this class of paints. Calcium tungstate is stated to yield an especially powerfully phosphorescent product.

Fire-proof paints. These paints differ widely in composition, but asbestos is present in nearly all; and many contain alkaline silicates, borax, ground fluorspar, glass, and similar substances. A mixture of aluminium and sodium silicates is sold under the name of 'fireproof cyanite.'

Water-proof or Damp-resisting paints. Lime, crushed flint and marble, sawdust, shellac, asphaltum, gutta-percha, residues from petroleum-distillation, and numerous other ingredients enter into the composition of these preparations, either in addition to, or instead of, the ordinary constituents of paint. One of the most efficient waterproof paints on the market at the present time is stated to be the product known as "Inertol."

Anti-fouling, Anti-corrosive, or **Preservative paints,** for surfaces of iron, ships' bottoms, &c. Many of these paints contain resinous constituents, and resemble varnishes in this respect. Oxide of iron, pitch, shellac, colophony, tannin, silicates, &c., are common ingredients of these compositions. An emulsion of tar and clay is stated to be a highly protective coating for iron and timber.

Water and Washable paints. Ordinary 'distemper' cannot be washed, but many of the water-paints on the market at the present time are washable when dry. Some are 'silicate of soda' preparations; in others, buttermilk, or casein is used in association with the colours. The miscibility of some with water is brought about or promoted by the presence of soap, or by the partial saponification of the oil. Water-paints merely require mixing with water, and those which are described as waterproof should resist atmospheric influences as satisfactorily as oil-paints.

Enamel paints. These are brilliantly coloured decorative paints, yielding smooth and lustrous coatings. Essentially they consist of oil varnishes, ground up with the finely divided pigments and thinned by spirit of turpentine. The high lustre of the painted surface is due to the large proportion of resins present.

Such miscellaneous products as the so-called ‘ gold ’ paints and enamels (consisting of bronze-powders suspended in resinous varnishes, or in a solution of celluloid in amyl acetate and acetone) ; ‘ silver ’ paint (in which finely divided aluminium is the pigment) ; aniline-coloured aluminium paints ; mica-scale paint ; flexible paint ; grease paints (tinted cosmetics) ; floor paints ; roof paints ; and the like, can receive but a bare mention here. Aluminium paint is now very extensively used.

For analysis of paints, *v.* ANALYSIS : also references below.

Literature.—J. Cameron, Oils and Varnishes, 1886 ; W. J. Russell and W. de W. Abney, Report . . . on the Action of Light on Water Colours, 1888 ; A. P. Laurie, Pigments and Vehicles of the Old Masters, Cantor Lectures, Soc. Arts, 1891–1892 ; J. Bersch, Die Fabrikation der Mineral-und Lackfarben, Wien, 1893 ; Evidence and Report, Departmental Committee on the Various Lead Industries, 1894 ; A. P. Laurie, Facts about Processes, Pigments, and Vehicles, 1895 ; R. Lemoine and C. du Manoir, Manuel Pratique de la Fabrication des Couleurs, Paris, 1898 ; G. H. Ellis, Analysis of White Paints, Chicago, 1899 ; F. H. Jennison, The Manufacture of Lake Pigments from Artificial Colours, 1900 ; J. Bersch (Trlr., A. C. Wright), The Manufacture of Mineral and Lake Pigments, 1901 ; A. H. Church, The Chemistry of Paints and Painting, 1901 ; J. C. Smith, The Manufacture of Paint, 1901 ; E. J. Parry and J. H. Coste, The Chemistry of Pigments, 1902 ; T. Oliver (ed.), Dangerous Trades, 1902 ; G. H. Hurst, The Painter's Laboratory Guide, 1902 ; E. G. Clayton, Some Analyses of Common Pigments, Chem. News, 85, (1902), 290 ; L. E. Andés (Trlrs. A. Morris and H. Robson), Oil Colours and Printers' Inks, 1903 ; A. C. Wright, Simple Methods of Testing Painters' Materials, 1903 ; P. N. Hasluck, Painters' Oils, Colours and Varnishes, 1905; F. Diolé, Les Matières Premières employées dans La Peinture en Batiment, Paris, 1905 ; A. H. Sabin, The Industrial and Artistic Technology of Paint and Varnish, 1905 ; J. M. Thomson, The Chemistry of Artists' Colours in relation to their Composition and Permanency, Soc. Arts Jour. 54 (1905–6), 388–397 ; C. H. Hall, The Chemistry of Paints and Paint Vehicles, 1906 ; G. Zerr und R. Rübencamp, Handbuch der Farben-Fabrikation, Dresden, 1906 ; A. P. Laurie, Oils, Varnishes, and Mediums used in the Painting of Pictures, Soc. Arts Jour., 55 (1906–07), 557–563 ; G. H. Hurst, Painters' Colours, Oils, and Varnishes, 1906 ; M. Toch, The Chemistry and Technology of Mixed Paints, 1907 ; J. G. Gentele (ed. A Buntrock), Lehrbuch der Farbenfabrikation, Braunschweig, 1906–09 ; Deutsche Gesellschaft zur Beförderung rationeller Malverfahren, Kommission zur Bekampfung von Misstaüden in der Herstellung, im Handel und in der Verarbeitung der Farben und Malmaterialien, München, 1906 ; G. Petit (trlr., D. Grant), The Manufacture and Comparative Merits of White Lead and Zinc White Paints, 1907 ; G. Zerr and R. Rübencamp (Trlr., C. Mayer), A Treatise on Colour Manufacture, 1908 ; C. D. Holley, The Lead and Zinc Pigments, 1909 ; J. C. Smith, Oxide of Zinc, Its Nature, Properties, and Uses, 1909 ; A. Eibner, Malmaterialienkunde als Grundlage der Maltechnik, Berlin, 1909 ; J. N. Friend, An Introduction to the Chemistry of Paints, 1910 ; W. G. Scott, White Paints and Painting Materials, Chicago, 1910 ; A. P. Laurie, Greek and Roman Methods of Painting, 1910 ; A. P. Laurie, Materials of the Painters' Craft, 1910. E. G. C.

PALATINE ORANGE. This colouring matter is the ammonium salt of tetranitro-γ-diphenol. It is soluble in water, and dyes wool and silk orange in a bath acidified with acetic or sulphuric acid (Hummel, Dyeing of Textile Fabrics (1885), p. 401).

Tetranitro-γ-diphenol $C_{12}H_4(NO_2)_4(OH)_2$ is obtained by the action of fuming nitric acid on γ-diphenol or on benzidine, and melts at 220° ; prolonged heating with concentrated nitric acid converts it into picric acid and oxalic acid (Schmidt and Schultz, Annalen, 207, 335).

PALISANDER WOOD. This name is now generally applied to one or more kinds of timbers that resemble rose-wood and are obtained in tropical South America and Mexico. The wood is lighter or darker violet brown or chocolate, and is marked by darker, often black, bands running with the grain. The actual origin of the timber is not known, but is attributed to the bignoniaceous *Jacaranda brasiliana* (Pers.) as well as to one or more species of the leguminous genera *Machaerium* and *Dalbergia.*

The name ‘ palisander wood ’ has apparently also been applied to an entirely different red dye-wood of unknown origin, obtained in Madagascar.

PALLADIUM. Sym. Pd. At. wt. 106·7. Occurs in all varieties of crude platinum and in many copper ores, especially in those which are nickeliferous and which are associated with pyrrhotine. It also occurs as an alloy with platinum or gold, especially in Brazil, and, in association with selenide of lead, in the Harz, in the form of hexagonal plates, although its normal crystalline form in other deposits is octahedral. Its principal source is the matte from the copper-nickel ores of Sudbury in Ontario. The total production of the United States, mainly from this source although partly from crude platinum, was over 2000 oz. in 1910.

Palladium has also been detected in a meteorite (Trottarelli, Gazz. chim. ital. 1890, 20, 611) and in the solar spectrum (Lockyer, Compt. rend. 1878, 86, 317).

Preparation.—Palladium may be precipitated as a double ammonium chloride from the mother liquor obtained after removing platinum and iridium (*v.* PLATINUM) (Wollaston, Phil. Trans. 1805, 95, 316). The pure metal may be obtained from the double salt by reducing the latter at a red heat in a current of dry pure hydrogen, after which the metal is cooled in a current of carbon dioxide to remove occluded hydrogen. The metal is also formed by the reduction of palladium chloride with formic acid or a formate. Mercuric cyanide precipitates palladium from neutral solutions as the white di-cyanide which yields the metal on ignition.

In either case the metal must be heated in hydrogen and then cooled in carbon dioxide.

Literature.—Bunsen, Phil. Mag. 1868, [iv.] 36, 253; Philipp, Dingl. Poly. J. 1876, 220, 95; Guyard, Compt. rend. 1863, 56, 1177; Leidie, *ibid.* 1900, 131, 888; Orloff, Chem. Zeit. 1906, 30, 714.

Palladium is a silver-white metal as hard as platinum but less ductile. It has a sp.gr. of 11·97 (Violle) and melts at 1546° (Waidner and Burgess, J. Soc. Chem. Ind. 1907, 1140). When heated to low redness in air, it becomes bluish, but it regains its white appearance at higher temperatures. At the melting-point of iridium, it boils and volatilises as a green vapour with partial oxidation.

It unites with fluorine and chlorine at a dull red heat, and superficially with iodine when treated with alcoholic iodine solution. Palladium is readily attacked by *aqua regia*, but less so by other acids. It unites with sulphur and selenium, less readily with phosphorus and arsenic, and with silicon at a white heat. It forms alloys with many metals.

Palladium has been employed for the graduated circles, &c., of philosophical instruments, and, to a small extent, in watch-making, and has been used for the electro-plating of parabolic mirrors on account of its silvery appearance and absence of change on exposure to impure air. It is also used for soldering platinum, but the bulk of the output is employed in the manufacture of dental alloys.

Palladium, in the form of palladium asbestos, is said to give excellent results when used as a contact substance in combustion analyses. It may be prepared for this purpose by precipitating a solution of pure palladium chloride in the presence of asbestos, by means of alkaline sodium formate (Jacobsen and Landesen, Ber. 1907, 40, 3217; Dennstadt, *ibid.* 3677).

Palladium, either in the form of sponge or black, has catalytic properties in a greater degree than platinum.

Literature on the catalytic properties of palladium and of colloidal palladium, Coquillon, Compt. rend. 1878, 87, 795; Phillips, Zeitsch. anorg. Chem. 1894, 6, 213; Lunge and Akunoff, *ibid.* 1900, 24, 191; Kraut, Ber. 1887, 20, 1113; Jahn, *ibid.* 1889, 22, 989; Zelinsky, *ibid.* 1898, 31, 3203; Bredig and Fortner, *ibid.* 1904, 3, 798; Paal and Roth, *ibid.* 1908, 41, 2273, 2282; *ibid.* 1909, 42, 1553; *ibid.* 1910, 43, 2684, 2692.

Palladium sponge or black would be employed on a commercial scale instead of or in conjunction with platinum if a sufficient supply were available.

Palladium absorbs various gases in quantities varying with its physical state (Cailletet and Collardeau, Compt. rend. 1894, 119, 830; Mond, Ramsay and Shields, Proc. Roy. Soc. 1897, 62, 290; Harbeck and Lunge, Zeitsch. anorg. Chem. 1898, 16, 50).

At ordinary temperatures, a palladium wire will absorb between 300 and 400 times its bulk of hydrogen and, when heated to redness in hydrogen, it absorbs nearly 1000 volumes and increases in bulk by nearly 10 p.c. This 'alloy' of hydrogen and palladium is permanent in air and *in vacuô* at ordinary temperatures, but yields up the whole of its hydrogen when heated *in vacuô* (Mond, Ramsay and Shields, Chem. News, 1897, 76, 317; Dewar, *ibid.* 274; Fischer, J. Soc. Chem. Ind. 1906, 993).

'Palladium hydrogen' is a valuable reducing agent (Sabatier and Senderens, Compt. rend. 1892, 114, 1430; Ann. Chim. Phys. 1896, 7, 357, 383; Engel, Compt. rend. 1899, 129, 518; Keiser, Ber. 1887, 20, 2323).

In presence of water and of oxygen, palladium hydrogen seems to behave as an oxidising agent, this being probably due to the formation of hydrogen peroxide, which in the presence of palladium, behaves as the oxidiser (Traube, Ber. 1889, 22, 1496; Hoppe-Seyler, *ibid.* 2215).

The salts of palladium have so far been but little applied to technical use, but some of them, like potassium palladium chloride, are employed for toning in photography (J. Soc. Chem. Ind. 1911, 1410). The metal is commonly included in the sub-group which includes the metals rhodium and ruthenium. All three are lighter, melt more readily and are more easily volatilised, oxidised, and dissolved than the other metals of the platinum group. The division of the platinum metals into two groups is, however, somewhat arbitrary, and depends mainly on difference in density; and palladium, like osmium, would almost require to be placed alone except as regards this one point, if subdivision were permissible.

Palladium Compounds.

Oxides. **Palladium monoxide** PdO may be prepared as an amber-coloured mass, yielding a black powder, by heating a mixture of a palladium salt with potassium carbonate; or as a bluish-green mass by heating the spongy metal in a current of oxygen at 700°–840°. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by hydrogen or hydrogen peroxide. When freshly precipitated in the cold from a palladous salt with sodium carbonate, the *hydroxide* is dark brown, and is readily soluble in alkalis. If dried or precipitated from a boiling solution it becomes insoluble. The *palladious* salts which correspond to this oxide, are of a green, red, or brown, colour, and have an astringent taste.

Palladium dioxide PdO_2 may be obtained in an impure hydrated form, soluble in acid, by the interaction of caustic soda and a palladichloride, or in a purer form, by the anodic oxidation of the nitrate (Wöhler and König, Zeitsch. anorg. Chem. 1905, 46, 323; *ibid.* 1906, 48, 203). It is a vigorous oxidising agent.

Palladium sesquioxide Pd_2O_3 is best prepared by the electrolytic oxidation of a concentrated solution of palladious nitrate at 8° with a current density of 0·5 cm. amp./cm^2; but if the electrolysis is prolonged, the dioxide is formed (Wöhler and Martin, *ibid.* 1908, 57, 398). It forms a dark brown unstable powder; gives unstable solutions in hydrochloric acid, and when suspended in ether and mixed with alkali chlorides, on addition of hydrochloric acid, the double chlorides $PdCl_3,2MCl$ are formed, which in contact with water yield the salts M_2PdCl_4.

Halogen compounds. **Palladious chloride** $PdCl_2$ may be prepared by the action of air or of chlorine and hydrochloric acid on the metal, or by heating palladious sulphide in dry chlorine (Matignon, Compt. rend. 1903, 137, 1051).

It crystallises with 2 mols. of water with a reddish-brown colour; loses water on heating and becomes dark brown, and at a red heat forms the *monochloride* PdCl, a red-brown crystalline deliquescent mass. Palladious chloride combines with carbon monoxide, yielding the crystalline compounds $PdCl_2 \cdot CO$, m.p. 197°; $PdCl_2 \cdot 2CO$, m.p. 142°; $2PdCl_2 \cdot 3CO$, m.p. 132° (Fink, Compt. rend. 1898, 126, 646).

Palladious chloride forms double chloride with other metals known as *palladiochlorides* or *chloropalladites* of the type M_2PdCl_4 (Gutbier and Krell, Ber. 1905, 38, 2385), of which the potassium salt is used in photography for toning (J. Soc. Chem. Ind. 1901, 154; Kessler, *ibid.* 849).

Many organic basic derivatives of these salts are known (Hardin, J. Amer. Chem. Soc. 1899, 21, 943; Rosenheim and Maass, Zeitsch. anorg. Chem. 1898, 18, 331; Gutbier, Ber. 1905, 38, 2105; Gutbier and Krell, *ibid.* 3869; *ibid.* 1906, 39, 616, 1292; Gutbier and Woernle, *ibid.* 2716).

Palladic chloride is not known in the free state, but only as double salts of the type M_2PdCl_6, and in combination with tertiary cyclic organic bases, and with tertiary bases, as intensely coloured products (Mohlan, Ber. 1906, 39, 861; Gutbier and Woernle, *ibid.* 4134).

The **sesquichloride** $PdCl_3$ is obtained as above, and in the form of double salts M_2PdCl_5 (Wöhler and Martin, *l.c.*). Bromides and iodides of palladium are also known (Gutbier and Krell, *l.c.*; Smith and Wallace, Zeitsch. anorg. Chem. 6, 380).

Ammonia salts. Ammonia acts on palladious salts forming *palladosammine* and *palladiodiammine* compounds, analogous to the corresponding platinum compounds (Müller, Annalen, 1853, 86, 341). Palladium derivatives of hydroxylamine (Zeisel and Nowack, Annalen, 1907, 351, 439) and of hydrazine chloride (Burdakoff, J. Russ. Phys. Chem. Soc. 1909, 41, 757) have been prepared.

When a 33 p.c. solution of a primary alkyl amine is added slowly to an excess of palladious chloride or bromide solution, rose-red needles of a salt $Pd(NH_3)_4X_2PdX_2$ are thrown down. These salts are readily converted into palladosammine derivatives of formula PdR_2X_2 (R=mol. of amine, X=halogen) by (*a*) heating to 200°, (*b*) by evaporating their aqueous solution, (*c*) by solution in warm alkali and precipitation with the desired halogen hydride.

The palladosammine chlorides are of a pale-yellow colour, the bromides dark-yellow, and the iodides brownish-yellow. They all yield colourless solutions in concentrated ammonium hydroxide (Gutbier and Krell, Ber. 1906, 39, 1292; Zeitsch. anorg. Chem. 1905, 47, 23). Certain diamines also yield rose- or flesh-coloured salts with palladous halides of the composition PdD_2X_2,PdX_2 (X=halogen, D=diamine) (Gutbier and Woernle, Ber, *l.c.*; *see* also Rosenheim and Maass, *l.c.*).

Palladious nitrate $Pd(NO_3)_2$ is formed by dissolving the metal or the oxide in nitric acid. It forms brownish-yellow deliquescent prisms, which on addition of water are converted into a brown powder of composition $Pd(NO_3)_2,3Pd(OH)_2$.

Potassium palladionitrite $Pd(NO_2)_4K_2$ is a pale-yellow crystalline powder formed by adding potassium nitrite to a hot solution of potassium palladiochloride, and according to Pozzi-Escot and Couquet (Compt. rend. 1900, 130, 1073), this may serve as a micro-chemical test for palladium.

Palladious cyanide is a pale-yellow salt obtained by the action of mercuric cyanide on a palladious salt.

Palladious thiocyanates are described by Belucci (Atti. R. Accad. Lincei. 1904, v. 13, ii. 386).

Palladious sulphate $PdSO_4,H_2O$, formed by the solution of the hydroxide in sulphuric acid, forms olive-green crystals which are decomposed by water forming a basic salt $Pd(SO_4),7Pd(OH)_2$.

The *sulphides* Pd_2S, PdS, and PdS_2; *selenides* (Roessler, Zeitsch. anorg. Chem. 1895, 9, 31; *see* Petrenko-Kritchenko, *ibid.* 1893, 4, 247), and also *thiosulphates* are known (*see*, too, Hofman and Höchtlen, Ber. 1904, 37, 245).

Palladium silicides are formed when the elements are heated together to 500°–600° (Lebeau and Jolibois, Compt. rend. 1908, 146, 1028).

A number of complex nitrites, sulphites, phosphates, and oxalates have been prepared (Loiseleur, Compt. rend. 1900, 131, 262; Vézes, Bull. Soc. chim. 1899, [iii.] 21, 172; Rosenheim and Itzig, Zeitsch. anorg. Chem. 1900, 23, 28).

For certain other organic compounds of palladium, *see* Hofmann and Rabe, *ibid.* 1897, 14, 293; Kurnakoff and Swosdareff, *ibid.* 1899, 22, 384. Z. K.

PALMITIC ACID $CH_3[CH_2]_{14}COOH$ is a constituent of the greater number of animal and vegetable fats, in which it occurs as the glyceride *tripalmitin* $C_3H_5(C_{16}H_{31}O_2)_3$. It is obtained from palm-oil (whence its name) by saponification; also by treating oleic acid with caustic alkali. It also occurs in Chinese wax (from *Sapium sebiferum* [Roxb.]), in Japanese wax (from *Rhus succedanea* [Linn.]), in butter, spermaceti, human fat, lard, &c. (Frémy, Annalen, 36, 44; Maskelyne, J. 1855, 519; Brodie, Annalen, 71, 159; Krafft, Ber. 1888, 2265; Varrentrapp, Annalen, 35, 210). Crystallises from alcohol in needles; m.p. 62°, and distils, with slight decomposition, between 339° and 356°, b.p. 268·5° (100 mm.); sp.gr. 0·8527 at 62°/4°.

Cetyl palmitate $C_{16}H_{31}O_2C_{16}H_{32}$ is the chief constituent of spermaceti (Heintz, Annalen, 80, 297). Crystallises from ether in thin plates; m.p. 53·5°.

Ceryl palmitate $C_{16}H_{31}O_2C_{27}H_{55}$ is the main constituent of opium wax (Hesse, Ber. 1870, 639); m.p. 79°. *Myricyl palmitate*

$$C_{16}H_{31}O_2C_{30}H_{61}$$

is found in beeswax (Brodie, Annalen, 71, 159); m.p. 72°.

By heating palmitic acid with glycerol, the mono-, di-, and tri-palmitins are prepared. *Tripalmitin* melts at 62° (Chittenden and Smith, Amer. Chem. J. 6, 230; Stenhouse, Annalen, 36, 54).

For estimation and other details, *v.* OILS, FIXED, AND FATS.

PALMITIN *v.* OIL, FIXED, AND FATS.

PALM KERNEL OIL. Palm kernel oil is obtained from the kernels of the palm tree fruit. The kernels are collected by the natives after the palm oil has been recovered from the fleshy part of the fruit; the shells are removed by cracking each nut separately with a stone or hammer. This work is chiefly done by women and children. Owing to the laboriousness of this process, and also to the fact that no more than about 15 pounds of kernels are obtained by one worker in a day, and that the kernels have to be carried to the market, enormous quantities of palm nuts are wasted. Although recently several nut-cracking machines have been sent to the west coast of Africa, they have hitherto not been able to supplant manual labour. The kernels are collected at the coast stations and shipped to Europe. The chief receiving ports are Hamburg, Liverpool, and Marseilles.

In Europe the kernels are screened to free them from shells, stones, nails, hammerheads, then passed over magnetic separators, and finally ground between rollers to a paste. The pulpy mass is either expressed in hydraulic presses or extracted with solvents. In the first process the meal must be pressed twice, on account of the large proportion of fat the kernels contain.

On a commercial scale, the first expression of palm kernel meal is carried out at a temperature of 45°–50°, the second at 55°–60°. Thus 43–45 p.c. of palm kernel oil is recovered.

The press cake contains 6–8 p.c. of oil; its proportion of nitrogen is small (about 2·5 p.c.), hence its value as cattle food is somewhat low. For the same reason the extracted meal has a low manurial value.

The colour of palm kernel oil is white to pale yellow. In the fresh state the oil is neutral and has a pleasant smell and an agreeable nutty taste. Commercial samples contain, however, notable amounts of free fatty acids.

For physical and chemical characteristics, *v.* tables under OILS, FIXED, AND FATS.

The chief constituent of palm kernel oil is lauric acid. In addition, there are present smaller quantities of caprylic, capric, caproic, myristic, palmitic, and oleic acids.

Palm kernel oil is largely used for soap-making. The freshest oil is employed in the manufacture of vegetable butter (like 'cocoa nut oil') and of 'chocolate fat.' In this latter manufacture a hard fat ('palm nut stearine') is obtained; the liquid 'palm nut oleine,' being a by-product, is used in soap-making.

J. L.

PALM OIL. Palm oil is obtained from the fleshy part of the ripe fruit of the palm tree *Elæis guineensis* (Jacq.), which forms vast forests along the west coast of Africa, extending between Gambia and St. Paul de Loanda. The west coast of Africa is practically the only supplier of palm oil. *Elæis guineensis* forms a very large number of sub-species for the description of which the reader may be referred to "Le Palmier a l'Huile" by Jean Adam (Challamel, Paris).

The favourite habitat of the palm tree is the open country or bushland; it grows frequently where the natives have cleared the virgin forest. The tree is characteristic of the coast line and the lower reaches of the rivers. It will grow in all soils, but does not bear well at a higher elevation than 3000 feet. Under favourable conditions the tree forms a trunk when five years old, and then begins to bear fruit. The yield afterwards increases and the tree gives its full harvest in its 12th year. This rate of yield is continued throughout the life of the palm tree, which lasts 50–60 years.

Owing to climatic conditions, the process of extraction has been hitherto practised exclusively by the natives, and is an exceedingly crude one. When the fruits ripen, the men climb up the trees and cut off the bunches with 'matchets.' Owing to the height from which the bunches fall, a large quantity of the fruit is bruised, which naturally leads to rapid fermentation and to hydrolysis of the oil. The women and children pick the fruit from the bunches and throw it into a hole dug in the ground and lined with leaves. The flesh of the fruit is at this time hard, and before the kernels can be separated, the flesh must be softened. This is done by sprinkling water on the fruit, covering it over with more leaves, weighted by stones and wood, and leaving for about two weeks. During this period, fermentation sets in, which causes the fleshy part of the fruit to become soft, so that the kernel—palm nut—can be removed more readily. This is done by men, who place the fermented fruits in a mortar, roughly made by lining a hole made in the ground with large flat stones. The fruit is then beaten with long wooden pestles, or the pulp is pressed by hand. The beaten pulp, together with the nuts, is taken out by women and children and placed over another hole, the sides of which have been cemented by plastering with a mixture of palm oil and wood ashes. The pulpy mass is then allowed to rest for a week. During this time, the oil drains into the cemented hole, from which it is ladled out into large calabashes of a size to make up one load.

The oil so prepared represents a superior kind of product. Women and children then pick out the nuts from the pulp, mix the pulp with water and place it in large iron cauldrons, where the whole mass is well boiled and stirred until the oil rises to the top. The oil is skimmed off, and, in some regions, mixed with the first extracted oil or put into separate vessels for the market. Finally, the residue is placed in a bag and squeezed over a hole so as to force out the liquid, from which more oil rises to the top. This oil contains a large quantity of water, and is again boiled out, skimmed off, and placed in calabashes.

The oil is carried—mostly by women—to the nearest coast or river station, where traders collect it in large barrels, and take it down to the coast station. There the oil frequently undergoes a rough purification by being boiled up with water, whereupon it is poured through sieves into barrels ready for shipment. During the last year, efforts were made to introduce European methods of manufacture in the coast stations as well as in the bush in the French, English, German, and Congo territories at the west coast of Africa.

Palm oil has a somewhat sweetish taste; in its perfectly fresh state it is used as a culinary fat in the villages of the west coast of Africa. Its odour is pleasant and resembles that of violets; this odour is not destroyed by bleaching with air at elevated temperatures, and persists even after the oil has been made into soap. In consequence of the very crude mode of producing palm oil, causing it to remain for a considerable time in contact with fermentable vegetable tissue, hydrolysis rapidly sets in, so that the oil on reaching the coast contains already a notable amount of free fatty acids. Palm oil when shipped from the coast has at least 10–12 p.c. of free fatty acids. The process of hydrolysis, once begun, continues in the barrels during the voyage, and in consequence, commercial palm oils, on arriving at their destination, contain frequently from 20–50 p.c., and even more, of free fatty acids. In such palm oils, free glycerol is found. In old samples the hydrolysis may even reach completion, so that such palm oil practically consists of free fatty acids (Lewkowitsch). The progress of hydrolysis can be observed even in oils kept in glass bottles.

The value of a palm oil in the market depends on the care with which it has been prepared, as also on the particular locality from which it is derived. The 'soft' oils are those containing a small quantity of free fatty acids, whereas the 'hard' oils contain a large proportion. The best 'soft' oils come from Lagos and Dahomey. Next in quality are the river oils ('medium' oils); whilst the lowest quality, the hardest oil, is represented by Congo oil.

The colouring matter of palm oil is not affected in the process of saponification by means of caustic alkalis or lime; in the acid saponification process it is destroyed. It is also slowly destroyed by exposure to air, more rapidly on heating or by bleaching with chemicals. The two latter processes are adopted in practice for preparing bleached palm oil.

The bleaching process most in vogue, and that giving the best results, is the dichromate process. The oil is freed from its gross impurities, and treated according to its quality with 1–3 p.c. of potassium dichromate and the requisite amount of hydrochloric acid. The dark 'chrome' liquor is then carefully run off, and the oil is washed with water, at first with the assistance of a little mineral acid, until it is quite free from chromium compounds and mineral acid.

Not all palm oils can be bleached successfully. Lagos and Old Calabar oils yield good results, but dirty-coloured red oils, such as Congo oil, have hitherto withstood all attempts to bleach them.

The chief constituents of palm oil are palmitin and olein. The proportion of stearin hardly exceeds 1 p.c. For the chemical and physical characteristics of palm oil, *v.* tables under OILS, FIXED, AND FATS.

Palm oil is chiefly used in the soap and candle industries. In the latter industry it is valued *cæteris paribus* by its 'titer.' Being a non-drying oil, it is also employed in the tinplate industry, to preserve the surface of the heated iron sheet from oxidation until the moment of dipping into the bath of melted tin.

For the purposes of the tin industry, 'palm oil greases' are sold, consisting of palm oil adulterated with cotton seed oil and mineral oil of the sp.gr. 0·905. J. L.

PALM RESIN or **CEROXYLIN** *v.* RESINS.

PALM SUGAR or **DATE-TREE SUGAR.** The liquid extract of certain palms is more or less rich in saccharine substances which are easily separated from such liquids. A method of obtaining sugar from this extract has existed in India from time immemorial, and was found to prevail among the aborigines of America on the discovery of that continent.

The palms which supply sugar are *Borassus flabellifer* (Linn.), *Phœnix sylvestris* (Roxb.), *Caryota urens* (Linn.), *Arenga saccharifera* (Labill.), &c.

Palm sugar is hygroscopic, and appears to be purgative if freely used. To divest it of this property it requires to be refined. The juice is sometimes obtained by cutting off the lower leaves of the crown about the end of October, and stripping the trunk of such as grow upon it to the place where incision is to be made. A bamboo cane is placed at the orifice each evening, by means of which the sap is conducted into vessels which are removed early next morning. In the case of *Phœnix sylvestris*, the tapping is done by making an incision in the wood at the base of the lowest green leaves, and subsequently removing slices of wood until the flow ceases. The cut axis of the inflorescence of *Caryota urens*, and the cut flower axes and cut sheathing spathes of *Borassus flabellifer* yield the sugary juice. The process of extracting the sugar from the sap must be proceeded with without delay, as fermentation sets in rapidly, when it is impossible to procure by boiling the syrup or *goor*, *i.e.* the mixture of molasses and crystallised sugar from which the sugar is extracted. The amount of sugar produced is about 40 p.c. of the syrup.

PALM TREE WAX *v.* WAXES.

PALYGORSKITE *v.* ASBESTOS.

PANCLASTITE *v.* EXPLOSIVES.

PANDERMITE. A natural calcium borate employed in the manufacture of enamels instead of borax, *v.* COLEMANITE.

PAPAIN or **PAPAYOTIN.** A vegetable digestive ferment obtained from the unripe fruit of *Carica Papaya* (Linn.), or papaw tree, and used as an alternate to pepsin, from which it differs by being active in neutral and alkaline conditions (*v.* E. J. Easter, Pharm. J. 1885, 45). The half-ripe fruit when scratched exudes a large quantity of a milky juice, which when dry forms a powder somewhat resembling gum arabic. The name 'papain' is usually restricted to the pure ferment associated with a proteid substance, and is obtained by precipitation with alcohol and separation of albuminous matter by basic lead acetate. The fruit of the papaw tree has long been used in the West Indies to render beef tender. The unripe fruit is split open and rubbed over the surface of the meat previous to cooking. Its action probably depends upon the fact that papain has a digestive action, not only upon muscular fibre, but also upon connective tissue. It digests fibrin and albumin in neutral and slightly alkaline solutions. When injected into the circulation in large doses it paralyses the heart. In smaller quantities it appears to favour the multiplication of micrococci in the blood (T. Lauder Brunton, Pharmacology, &c., 927).

PAPAVERINE *v.* VEGETO-ALKALOIDS.

PAPAVEROSINE *v.* VEGETO-ALKALOIDS.

PAPER. The art of modern paper-making consists in uniting or 'felting' together any fibrous vegetable matter, so as to form a continuous sheet. Owing to the abolition of the paper duties, in 1827, and the consequent rapid growth of cheap literature, the old dictionary definition of paper as 'a substance made of linen or cotton rags' no longer holds good. As a matter of fact, these substances constitute but a small fraction of the raw materials of the paper-maker.

Any vegetable substance possessing a sufficiently fibrous structure can be utilised. Occasionally both animal and mineral fibrous substances—such as wool, silk, or asbestos—are employed, either alone or as admixtures.

In order to give some idea of the variety of materials from which paper can be or has been manufactured, we may cite a book that was published at Regensburg, Germany, by Jacob Schaeffer in 1765, the paper of which was made from about sixty different sources, amongst which the following are curious and interesting: sawdust, hop-vines, hornets' nests, peat, straw, cabbage-stumps, moss, various woods, thistle-stalks. In the majority of cases the paper is of very inferior quality, the pulp being coarse and unbleached. A similar book is that containing the poems of the Marquis de Villette, published in 1786. Another, of historical interest, is one the paper of which was made entirely from straw. It was published in England in 1800.

Notwithstanding the variety of materials available, rags of various kinds continued to form the chief raw material of the paper-maker until the year 1860, when Mr. Thomas Routledge introduced esparto grass (*v.* ESPARTO). This material, which possesses many advantages, is very extensively used in this country. Of late years, however, owing to the enormous increase in the demand for paper, it has been largely supplemented by straw, and more especially by wood.

The chemical characteristics of the paper-makers' raw materials have already been discussed in the article Cellulose. These materials consist, with the exception of cotton and linen rags, of one or other, or a mixture, of the various compound celluloses; and the treatment they undergo consists essentially in isolating the cellulose by chemical means. This treatment is accompanied by separation, more or less complete, into individual cells, which vary in length from about 1·5 mm. in the case of esparto to 30 mm. in the case of flax. This chemical splitting up into cells is supplemented by a mechanical operation known as 'beating,' whereby the material is still further reduced (*v. infra*).

The various processes that the different forms of cellulose undergo before being made into paper may be divided into four main branches—(1) cleaning, (2) boiling, (3) bleaching, (4) beating, or reducing to pulp. In addition to these, there are the processes of sizing, colouring, &c., which will be included in No. 4.

1. **Cleaning.** This is a purely mechanical process, and consists in removing from the raw material adventitious matter, such as sand, dirt, &c. Part of this work is done by hand-labour, especially in the case of rags, but the modern tendency is to replace hand-labour as much as possible by machinery. In the case of rags cut by machinery, the pieces, spread on to a table made of coarse wire gauze, are examined by girls, and such articles as buttons carefully removed. At the same time the rags are sorted into various kinds, such as cotton, linen, jute, canvas, &c., each kind being separately stored in boxes. This process, which is somewhat costly, is only practised in the case of rags intended to be used for high-class paper. The usual plan, which may also supplement the hand-labour, is to pass the cut rags through a 'willow.' This consists of two wrought-iron drums, furnished with teeth, which, when the drums revolve, pass rapidly near stationary teeth fixed in the frame in which the drums work. The sides and top are covered in with iron doors, and underneath is a grating for the escape of dust. The rags are fed into the drums by an endless travelling platform, and pass from thence into a duster, consisting of a kind of hollow cylinder made of iron bars covered with wire cloth. The cylinder revolves almost horizontally, a slight dip being given to it in order that the rags may be carried forward to the lower end. The 'willows' used for esparto and various other fibres are similar in principle. The cleaned and dusted rags, or other material, are carried forward by an endless felt to the boilers, where the next operation is performed.

2. **Boiling.** The boiling processes vary considerably with the kind of material. We will discuss them in the order of their simplicity.

(*a*) *Rag boiling.* Rags, being for the most part refuse from textiles made from pure or nearly pure cellulose, require a comparatively light treatment. It may be conducted either in spherical or cylindrical boilers, or in the 'vomiting' boilers, described under Esparto. In the case of spherical boilers the heating is caused by 'live' steam: cylindrical boilers are usually jacketed. It is preferable to cause the boilers to revolve. They are furnished with inlet and outlet steam-pipes, pipes for running in liquor and water, man-holes for filling and emptying, and safety valves, pressure gauges, &c. The alkali employed may be either caustic soda, caustic lime, sodium carbonate, or a mixture of the latter. The proportion of alkali depends mainly on the state of the rags and the nature of the substances to be removed, and also to some extent on the pressure of steam employed and the duration of the operation. As a general rule applicable to rags and all other fibres, it may be stated that the higher the pressure and the longer the time occupied, the less alkali (within, of course, certain limits) is necessary. The amount of alkali varies from 1 p.c. of 70 p.c. caustic soda in the case of the higher qualities of rags to 5 p.c. in the case of lower qualities.

The pressure also varies considerably—say, from 5 to 60 lbs. per square inch. In the opinion of some the lower pressures are to be preferred, as at the high temperature associated with higher pressure there is a tendency to fix a certain amount of dirt and colouring matter in the rags, thereby defeating to some extent the object of the boiling. After boiling, the rags may be washed in the boiler or in a separate washing engine which will be subsequently described.

An effective method consists in exposing the rags, continuously wetted with caustic soda solution, to an atmosphere of steam at 10 lbs. pressure. The dry and dusted rags are packed into waggons, fitted with perforated bottoms. The waggons are then run into a horizontal cylindrical vessel, called a 'kier,' which they almost completely fill. When in position, a pipe at the bottom of each waggon fits tightly over a pipe passing through the bottom of the kier and connected by means of a centrifugal pump with an outside pipe communicating with the top of the kier. Caustic soda solution is run in, and is made to circulate through the rags by means of the pump. One end of the kier is closed and the other is fitted with a V-shaped door, which falls into a slot of similar shape, making a readily-adjusted steam-tight joint. The door is raised and lowered by hydraulic pressure. The apparatus is known as the 'Mather Steamer Kier.'

(*b*) *Esparto boiling.* Esparto, being a compound cellulose, requires a more drastic treatment than rags. The first process that esparto undergoes is that of 'picking.' This operation, which is done by hand, consists in removing root-ends, weeds, &c. It has latterly been largely dispensed with, and a more complete mechanical treatment substituted. For this purpose the grass is passed through a willow and duster similar in principle to that described under the head of Rags.

After passing through the machine the grass is in some cases carried along a travelling belt, and is discharged direct into the boiler. These are almost invariably stationary, as a revolving boiler is apt to cause the grass to form into dense masses, which resist the action of the soda used in boiling. An esparto boiler is shown in Fig. 1. It is furnished with a perforated false bottom B, on which the grass rests. Steam enters by the pipe A, which reaches below the false bottom and causes the liquor to rise up the outer pipe C, strike against the 'bonnet' D, and distribute itself over the grass in a fine spray. The door E is for filling in the grass, and the door H for emptying. The boiler is fitted with a safety valve K. Each boiler holds about 60 cwt. of grass, and the operation lasts about five hours. The amount of soda varies according to the nature of the esparto, Spanish requiring less than African: about 16 lbs. of 70 p.c. caustic per cwt. is an average quantity. The steam pressure also varies from 5 lbs. to 45 lbs. per square inch. Occasionally an open boil is used. The modern tendency is to employ the higher pressures, as being more economical of time and soda. Other forms of vomiting boilers have lately been introduced, in which the vomiting arrangements are fixed either outside the boiler altogether, as in Roeckner's, or are placed at the sides, as in Sinclair's, thus giving more space for the grass. The alkali used is invariably soda. The boiling operation being completed, the liquor is run off from a cock at the bottom of the boiler, and the grass partially washed with water in the boiler. This also has the effect of cooling the grass and enabling the workmen to remove it to the washing engine or 'breaker.'

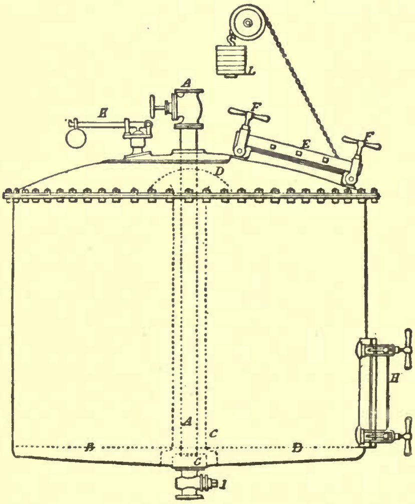


FIG. 1.

In some mills the grass is placed in a series of tanks similar to those used for dissolving black ash, where the washing can be effected with a very small quantity of water—a very important matter from the point of view of recovery of the soda.

The washing engine, which may be used for any other fibres besides esparto, is shown in Fig. 2. It consists of a rectangular vessel with rounded ends, in the centre of which is the mid-feather B. The action of the roll A, which is fitted with clusters of steel knives G, disintegrates the grass and causes it to circulate round the engine. The floor is sloped as shown by the dotted lines D and D′, the effect being to cause the grass to pass under the roll A, the knives of which pass close to similar stationary knives fixed to the 'bed-plate' I. The distance between the roll and the 'bed-plate' can be varied at will by means of the wheel E.

A continuous stream of water is run into the engine, and the dirty water is lifted by means of the 'drum washer' C, the periphery of which is covered with fine wire gauze. The centre of the drum is formed of a conical tube, the narrow end of which is towards the 'mid-feather.' The dirty water passing through the wire gauze is lifted by the bucket-like compartments O, and is discharged through the centre of the drum, whence it is led away by the trough L, and passes down the 'mid-feather,' which is made hollow for the purpose.

The grass having been thoroughly washed and reduced to the state of pulp by means of the steel knives in the roll, is ready for bleaching. This operation will be described subsequently.

(*c*) *Straw boiling.* Straw closely resembles esparto in its chemical characteristics, but being more highly lignified a somewhat severer treatment is required. This is obtained either by boiling at a very high pressure, 60–80 lbs., or by using a larger proportion of caustic soda (18–20 lbs. per cwt.). In treating straw for use in high-class papers, it is customary to blow it through a large receptacle, the floor of which is covered by a sieve kept in vibratory motion. The receptacle is arranged that heavy particles, such as sand or stone, fall through the grid in the first section, while the heavier particles of straw, such as the knots, are carried forward to the second section. The very light pieces are carried through to the third section.

The advantages of this system of treatment are, that the subsequent operations can be conducted with greater uniformity. The boiling operation usually takes place in large revolving boilers. Owing to the rotary action of the boiler, the straw is in the state of fine pulp and readily flows through a 3-inch pipe. It is run into tanks, the bottoms of which are formed of perforated tiles. The liquor is run off and fresh water added until all soluble matters have been removed. It is then ready for bleaching.

In making straw pulp of fine quality it is sometimes found advantageous to pass the washed pulp between horizontal revolving stones, whereby the knots and any unboiled portions are finely ground and rendered more easily bleached.

(*d*) *Wood v.* CELLULOSE.

(*e*) *Other fibres.* There are a number of fibrous materials which are available for the paper-maker, such as jute, manilla, adansonia, &c., the treatment of which calls for no special notice. The nature of the treatment which they undergo varies with the kind of paper for which they are intended. The greater number of such fibrous materials are used for papers where strength is of far greater importance than colour or appearance, such, for example, as brown papers and packing papers. In such cases the paper-makers aim at a minimum resolution of the fibre, so as to preserve the strength and increase the yield. In the case of jute the individual fibres are very short and weak, and a strong and perfectly white paper made from jute is an impossibility. If, however, the filaments are not completely resolved, a strong fibre can be obtained.

The cheapest method of preparing such fibres is to boil them under pressure with milk of lime. This treatment is not nearly so effective as that with caustic soda, and the fibre produced is coarse and hard. The yield is, however, high.

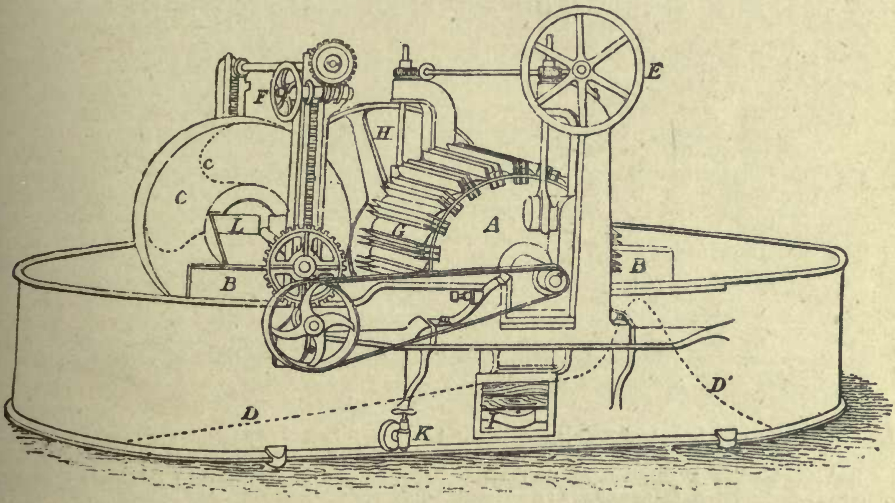


FIG. 2.

There is another very important material which may be mentioned here, viz., mechanical wood-pulp. A large quantity of this is used in the cheaper kinds of paper. It is prepared by disintegrating wood by mechanical means alone. Blocks of wood, from which the knots have been removed, are pressed against revolving stones; at the same time a stream of water flows on to the stones. The wood is so placed that the fibres are torn off in the direction of their length in order to secure as great length as possible. The stream of water carries the pulp forward as fast as it is made. The larger undisintegrated portions are removed by screens of coarse wire cloth. In order to still further refine the pulp it is caused to pass between two horizontal cylinders of sandstone, the upper one of which revolves rapidly.

Where power is cheap such pulp can be economically prepared; it is, however, at best but a poor substitute for esparto and other pulps. Paper made with it has but little strength, and is very susceptible to atmospheric action. The woods chiefly used are white pine and aspen; the latter yields a pulp of good colour but little strength.

3. **Bleaching.** The processes of bleaching paper-pulp are practically identical for all classes of material. The agent employed is a solution of calcium hypochlorite, made by dissolving bleaching-powder in water. The operation may be conducted in the breaking engine previously described, or in a separate engine called a 'potcher,' which is similar in construction, but the roll is furnished only with blunt blades, which serve as paddles to cause the pulp to circulate. Sometimes large potchers made of brick and cement are used.

A system that is being very largely used, is that known as the 'Continuous Bleaching Process,' where the bleaching is carried on in a series of towers (*v.* Fig. 3). The pulp, after washing and breaking, is pumped into the first tower, and after partial removal of the water by means of a concentrator, is bleached while being kept in circulation by means of a centrifugal pump placed at the base of the tower. If only one tower is in use, the stuff can be pumped up continuously to the top of the tower, where it is distributed by means of a cone towards the sides. Where there is a series or 'battery' the pulp is pumped up into the next tower, and so on through the series. It is usual to have a second concentrator fitted to the last tower for the purpose of removing the spent bleach, and the soluble non-cellulose constituents.

The advantages claimed for this system are (1) comparatively little power is required for circulating the stuff, (2) an approximate saving of bleach, equal to 25 p.c. owing to the concentration of the pulp under which the bleaching process is carried out, (3) the bleaching is carried out at the ordinary temperature, thus obviating any possibility of tendering the pulp.

The action of the calcium hypochlorite may be hastened by heat, the 'potchers' being provided with steam pipes for this purpose, or by the addition of sulphuric or hydrochloric acids. The best results are obtained by the action of bleaching solution alone, in which case a longer time must be given. This is more than compensated for by the extra yield of pulp and its greater strength.

The amount of bleaching-powder necessary to bleach well-boiled pulps varies from about 7 p.c. in the case of straw to about 15 p.c. in the case of wood. These amounts are calculated on the unboiled materials.

Chlorine gas as a bleaching agent was formerly used for rags, but is now almost entirely superseded. As a matter of fact, chlorine will not bleach the majority of pulps; it enters into combination with the fibre substances, producing yellow-coloured combination products. Advantage has been taken of this fact by F. C. Glaser in his process for treating straw. The straw is first boiled with a reduced quantity of soda; it is then drained and exposed to the action of chlorine gas. A subsequent treatment with bleaching liquor produces a very pure white pulp.

The bleaching of pulp by means of the products of the electrolysis of chlorides has attracted much attention. Of the various processes introduced, one of the best known is that of M. Hermite, which is in successful operation in many mills on the Continent. It depends upon the fact that when a solution of magnesium chloride is electrolysed, magnesium hypochlorite is formed, which possesses considerably greater bleaching efficiency than calcium hypochlorite of equal chlorine strength.

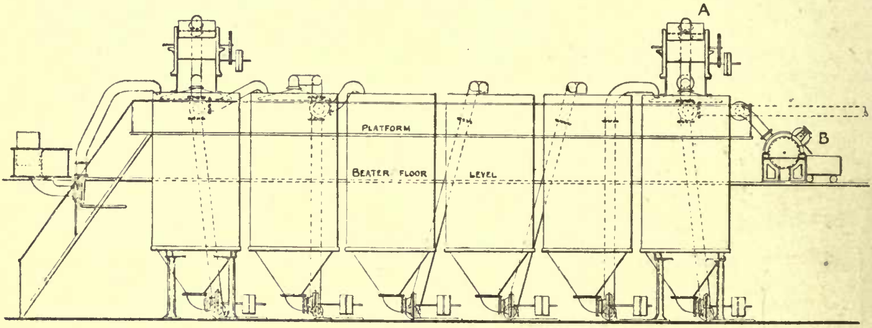


FIG. 3.

After bleaching, and before the next operation of beating, the pulp is sometimes purified by passing it over a 'presse-pâte,' which consists of a strainer and that part of a paper machine on which the web of paper is formed. The pulp is thus made into a thick continuous sheet; at the same time all soluble impurities, such as calcium chloride, &c., are removed.

The 'presse-pâte' system has latterly been largely superseded by the use of 'concentrators' such as the 'Couper' concentrator.

This consists of a revolving drum fitted with a central cone arranged so as to deliver water at both ends. The drum is of perforated brass and covered with wire-cloth. The pulp is pumped through a butterfly throttle valve into a splaying mouth, whereby it is caused to flow along the whole width of the drum cover. The cover or hood is so arranged by means of packing, that the water in the beaten stuff can be forced through the wire-cloth of the revolving drum, at a pressure of 2–3 lbs. to the square inch, leaving a mat of fibre upon it. The fibre is then picked off the wire by means of a jacketed couch roll, and again removed by means of a wooden doctor, and deposited into boxes.

This action secures a higher concentration of pulp than the 'presse-pâte,' as in the latter case the water is separated from the fibre by gravity only.

4. **Beating.** The bleached pulp, before being made into paper, requires to be beaten up into fragments of from 1–2 mm. in length. In the case of esparto, straw, and wood, this length represents that of the individual fibres; the beating operation, therefore, is confined to completing the disintegration produced by the boiling and bleaching processes. But in the case of cotton and flax, the individual fibres of which are about 30 mm. in length, a much more extended mechanical treatment is necessary. The operation is conducted in an engine called the 'beating engine,' similar in construction to the breaking or washing engine already described (Fig. 2), the only important difference being that the roll of the former is furnished with a larger number of knives.

The distance between the roll and the bedplate is arranged so as to 'tear' the fibres, instead of 'cutting' them, so as to give them the maximum amount of felting power. In some cases the knives are made of bronze in order to avoid contamination of the paper with iron-rust. Various other forms of beating engines have lately been introduced which differ somewhat in the arrangement of the various parts, but which do not call for special notice.

It is in this stage of the treatment of the pulp that the various loading, sizing, and colouring materials are added. Before doing this, however, it is necessary, unless the operation has been previously performed in the washing engine, to remove the excess of bleaching solution. This may be done by simple washing, many beating engines being provided with washing drums for the purpose; or the bleach may be neutralised by the addition of an antichlor, such as sodium sulphite.

5. **Loading.** Most papers, except perhaps the very finest 'writings,' contain some added mineral matter, such as 'pearl-hardening' (calcium sulphate, ground or precipitated) for the better qualities, and china clay for the cheaper papers. This addition cannot, unless carried to excess, be considered an adulteration, as it fills up the pores of the paper, and enables it to take a better surface under the calender.

Sizing. All writing papers, and most printing papers, require to have some material added to them that will enable them to resist ink. This can be done in two ways—viz., by engine-sizing and tub-sizing: the former is done in the engine itself, the other in the finished paper. Engine-sizing consists in the addition of resinate of aluminium, which is precipitated in the pulp by the mutual decomposition of resinate of sodium, prepared by dissolving rosin (colophony) in sodium carbonate, with a solution of alum or aluminium sulphate. In addition to the resinate of alumina most papers contain starch, which may be dissolved in water and mixed with the resinate of soda, or may be added undissolved: the former is the plan usually adopted. Almost all papers, even blotting papers, contain starch, which assists in binding the fibres together, but has little or no sizing property, and therefore does not prevent the paper being absorbent. The amount of alum added to pulp is largely in excess of that necessary to fully precipitate the resin; the excess appears to be necessary in order to get a hard paper. It probably has some action on the cellulose itself. The excess, moreover, tends to brighten the colour of the paper.

Tub-sizing. This consists in passing the finished paper, either in the form of sheets or in the web, through a solution of gelatin to which alum has been added. Occasionally soap is added to the gelatin. When alum is added to a solution of soap and gelatin, the soap is decomposed and an infinitely fine precipitate is produced, which forms with the gelatin a kind of emulsion. The addition of the soap enables the paper to take a high surface with a minimum of pressure under the calender.

6. **Colouring.** Most bleached pulps have a slight yellow tinge which requires to be complemented by the addition of blue and pink in order to produce a perfectly white paper. The blues usually employed for this purpose are ultramarine and smalts, and occasionally aniline blues; the pinks are either preparations of cochineal or aniline. For the production of coloured papers a variety of different colouring matters are employed in addition to those mentioned, such as Prussian blue, chrome yellow, Venetian red, &c.

The addition of the loading, sizing, and colouring materials proceeds at the same time that the pulp is being 'beaten.' When this is completed the pulp is ready to be made into paper.

7. **Making into paper** (*Hand-made paper*). This is made on a mould of wire-cloth, furnished with a moveable frame of wood called a 'deckle,' extending some distance above the surface. The workman dips the mould with its 'deckle' into a vat containing the beaten pulp largely diluted with water, and removes more or less pulp, according to the thickness of paper required. He, then, by dexterous lateral movements causes the fibres to unite and form a continuous sheet; at the same time the excess of water drains away. The 'deckle' is then removed, and the wet sheet of paper transferred to a piece of felt. This operation is continued until a number of sheets of paper and pieces of felt have accumulated, forming what is called a "post." They are placed in a press to remove a further quantity of water. The sheets are then passed through a solution of gelatin, and hung up on lines or poles to dry. When dry the sheets are calendered.

Comparatively little paper is now made by hand on account of the great expense of labour; it is, however, preferred for bank-notes, drawing-paper, &c., on account of its uniform strength. Owing to the fact that a shaking motion in every direction can be given to the mould, the fibres are irregularly distributed, and the maximum of felting power is obtained, whereas in machine-made paper, as will be seen subsequently, the fibres tend to place themselves in the direction in which the stream of pulp flows. Such paper, therefore, is strongest across the web.

Machine-made paper. The modern Fourdrinier paper machine, so-called from the original inventor, consists essentially of an endless mould of wire-cloth on to which a continuous stream of pulp flows and on which a continuous sheet of paper is formed. On leaving the wire-cloth the wet sheet of paper passes through a series of rollers and over heated cylinders and calenders whereby it is dried and finished. The machine is shown in side elevation Figs. 4 and 5.

The pulp on leaving the beaters flows into a large store vessel called a stuff-chest where it is diluted to the proper consistency with water. It is furnished with agitators to keep the pulp uniformly distributed. From here it is pumped and delivered under a constant head, to the sand tables. These consist of a long series of shallow troughs, the bottoms of which are covered with pieces of felt or thin strips of wood placed across the direction of the stream of pulp and at a slight angle, the object of which is to retain any particles of sand or dirt. The pulp passes from the sand tables to the strainers, which are usually of the revolving type, and like the old flat type of jog strainer or knotter consist of strong bronze plates having a large number of fine V-shaped slits cut in them. The slits are from 2–3 inches long, and vary in width from 0·007 to 0·05 of an inch. These slits allow only the fine fibres to pass, retaining all unboiled or unbleached portions of fibre or other impurities. The passage of the stream of pulp through the slits is assisted by giving a vigorous shake to the strainer plates or by means of a pump placed below. One of these strainers is shown at *c*; the shake is produced by the cam *a* acting on the hammer *b*.

The strained and purified pulp passes from the strainer on to an endless travelling wire-cloth which is carried by a large number of small rolls *f''* and by the large rolls F *f'* and G. The amount of pulp flowing, and consequently the thickness of the finished paper, is regulated by the sluice *e*. The thickness also depends upon the rate at which the wire-cloth travels; it may vary from 60 to 600 feet per minute.

Travelling with the wire-cloth are two endless thick india-rubber bands *i* called 'deckle straps.' These can be regulated at any distance from each other and serve to determine the width of the sheet of paper. The rolls *f''* and the wire-cloth are carried by standards *g''* which are jointed at their lower ends. At the top they are connected with a rod having a rapid to-and-fro motion which is communicated to the wire-cloth. This shaking motion serves to some extent to neutralise the tendency of the fibres to set themselves in the direction of the flow of the pulp.

The small rolls *f''* cause the excess of water to pass more freely through the wire-cloth. As the sheet of paper passes along, it goes over the vacuum boxes I which are connected with air-pumps, by which a further quantity of water is removed from the sheet of paper.

Underneath the wire-cloth is a box K called a 'save-all.' The water passing into it holds in suspension a certain amount of fibre. This fibre can be recovered by passing the water through a filter or the water may be used to dilute a fresh quantity of pulp. Any pattern, or 'water-mark' as it is called, may be produced on the paper by causing a light skeleton roll, called a 'dandy roll' covered with raised wire in the form of the pattern required, to press lightly on the wet paper. It is generally placed between the vacuum boxes I. After passing the last box I the still wet paper passes between the 'couch-rolls' GG'. These are covered with felt and serve by their pressure to still further dry the paper. The paper here leaves the wire-cloth and is transferred to an endless felt which travels in the direction of the arrows over the roll *k*. On its journey, it passes between the 'first-press rolls' K, and then through the 'second-press rolls' L. The paper, being still weak, is supported by a felt travelling on the rolls *l*. After leaving the 'second-press rolls' L, the paper is carried to the drying cylinders M, heated with steam, of which there may be as many as twelve or more.

They are generally divided into two sets, between the sets being a pair of highly polished heated rollers N called 'smoothers.' After leaving the last drying cylinder the paper passes through the calender O and is then wound off at P.

Single cylinder machine. In the single-cylinder or 'Yankee' machine, the paper after having been formed on a wire cloth in substantially the same manner as in the Fourdrinier machine, is dried by passing over one very large cylinder.

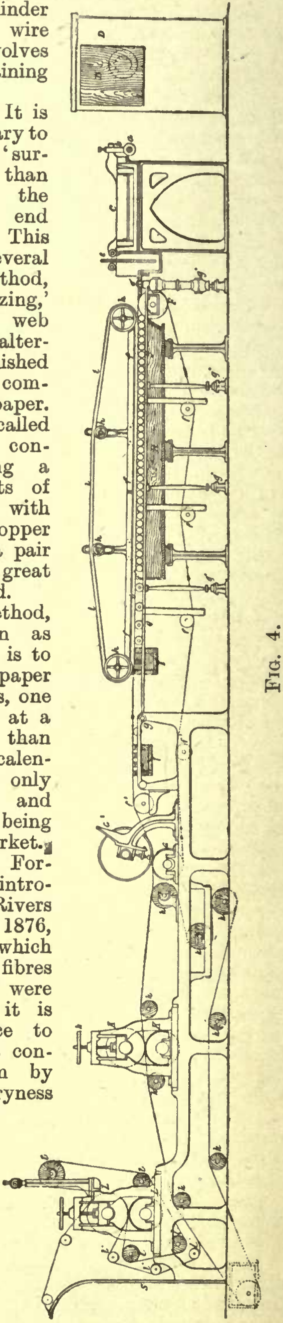


FIG. 4.

In another form of machine the paper is formed on the periphery of a cylinder covered with wire cloth, which revolves in a vessel containing the pulp.

Calendering. It is sometimes necessary to give a greater 'surface' to a paper than is acquired by the calender at the end of the machine. This may be done in several ways. One method, called 'web-glazing,' is to pass the web of paper between alternate rolls of polished iron and highly compressed cotton or paper. Another method called 'plate-glazing,' consists in passing a bundle of sheets of paper alternated with polished zinc or copper plates, between a pair of rolls to which great pressure is applied.

Still another method, which is known as 'friction-glazing,' is to pass the web of paper between two rolls, one of which travels at a much higher rate than the other. After calendering, the paper only requires cutting and sorting before being placed on the market.

Soda recovery. Formerly, before the introduction of the Rivers Pollution Act of 1876, all liquors in which esparto and other fibres had been boiled were thrown away; it is now the practice to recover the soda contained in them by evaporating to dryness and incinerating the residue, thus obtaining the soda in the form of carbonate. This has in most cases been found to be highly remunerative. Various forms of apparatus for economically evaporating large quantities of water have from time to time been introduced. These can be divided into two types, (1) the direct evaporating plants under ordinary atmospheric pressure, and (2) single or multiple effects, where evaporation is carried on under a partial vacuum. A very effective form representing the first type is that known as the Porion evaporator, which consists of a large brick chamber on the floor of which the liquor is placed. A number of rapidly revolving fanners stir up the liquor and distribute it in the form of a very fine spray. The chamber is connected with a reverberatory furnace where the evaporated product is incinerated, the waste heat from which serves for the preliminary evaporation. This evaporator, working with fairly strong liquors, is capable of producing 1 ton of recovered soda for an expenditure of about 27 cwt. of coal.

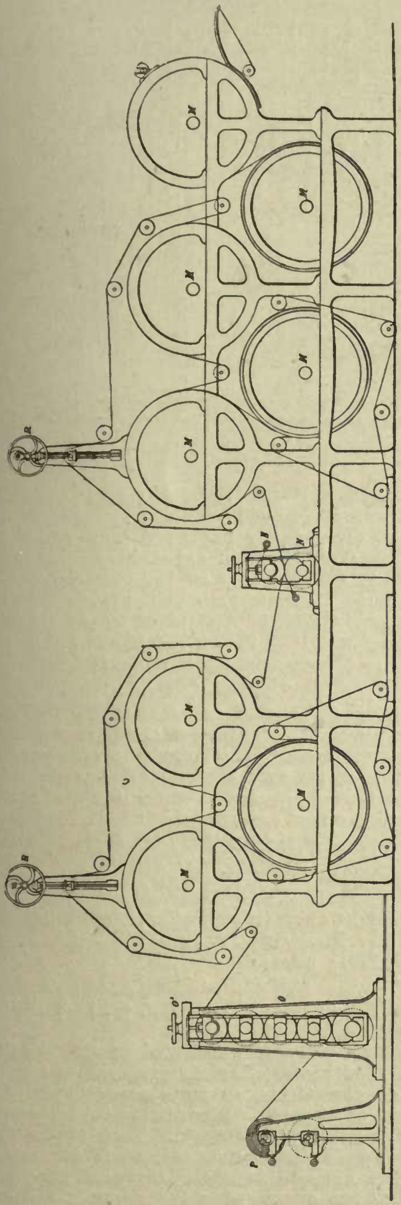


FIG. 5.

There are several forms representing the second type, one of the best of which is that known as the 'Scott Multiple Effect Evaporator.' By means of this apparatus, coupled with a rotary furnace, it is possible to effect recovery of 95 p.c. of the soda, and with a coal consumption equal to 10 cwt. per ton of ash produced.

One form of the evaporating plant is shown in Fig. 6, and may consist of one or more vessels. Each unit consists of an evaporator, the heating surface of which is in the form of tubes of two different diameters so arranged that the liquor which circulates in these tubes does so with considerable velocity, thus exposing a large heating surface. The steam generated in the first effect, working under a pressure of 4–5 lbs., is used to heat the second 'effect' which works under a slight vacuum, and so on for each consecutive unit, with a correspondingly increased vacuum.

The 'black' liquor is supplied to the first 'effect' and passes gradually through each succeeding 'effect' until it becomes so concentrated that it will only just flow.

The concentrated liquor is pumped up to a store tank mounted above a roaster, which may be of the flat hearth type or better still, a rotary roaster. The latter is a revolving steel shell provided with steel rails, and supported on steel wheels, some of which act as 'supports' and others as dividers. The inside lining of fire brick is so arranged that a slight slope is given from the feeding end to the discharging end. The concentrated liquor is fed into the roaster at a constant rate, the temperature of the roaster being at white heat. This causes immediate evaporation and firing of the organic matter. The fused sodium carbonate is carried forward to the end of the roaster, and is ultimately discharged as a dark incandescent mass into barrows placed at the end of the furnace. The contents of the barrows are left to burn slowly when the product is almost quite white.

The Yaryan evaporator is similar in principle to that already described. An important advantage of these evaporators is the fact that the liquors, excepting while in the incinerating furnace, are not in contact with the products of combustion of the fuel employed. Moreover, the bulk of the water evaporated is recovered in the form of distilled water.

The recovered soda, which, as has been said, is in the form of carbonate, may contain in addition a considerable quantity of potash, derived from the fibrous substances which have been boiled in it; also in the case of straw or esparto, a large proportion, as high as 7 p.c., of silica. It is dissolved in water and causticised by boiling with lime, when almost the whole of the soda it contains is recovered in the form of sodium hydroxide. It should be borne in mind, however, that it is liable to contain various accumulated impurities such as sulphate and chloride, &c., derived from the soda originally employed, and from that which has to be added to make up the loss in evaporation. This loss, together with that due to soda retained in the fibre, leakage, soda volatilised during calcining, and soda left in the lime mud after causticising, invariably amounts to 5–10 p.c. It is important that the loss should be made up with as pure a form of alkali as possible.

E. J. B. and W. B.

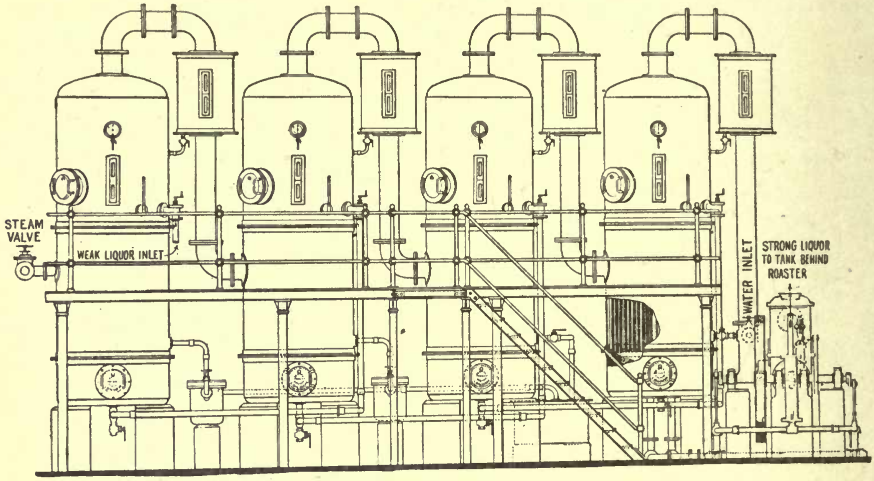
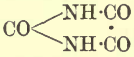


Fig. 6.

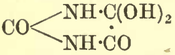
PAPER-COAL. A synonym for Dysodile (*q.v.*).

PARABANIC ACID (*Oxalylcarbamide*)



$$CO<\begin{array}{l}NH\cdot CO\\ \quad\;\;\cdot\\ NH\cdot CO\end{array}$$

prepared by the oxidation of uric acid with moderately concentrated nitric acid (Liebig and Wöhler, Annalen, 1838, 26, 285; Strecker, Annalen, 1861, 118, 151; Tollens, Ber. 1872, 5, 801), with hydrochloric acid and potassium chlorate, with manganese dioxide and hot dilute sulphuric acid, or with bromine and water; or by oxidising guanine with hydrochloric acid and potassium chlorate (Fink, Annalen, 1864, 132, 298); has been synthesised by heating oxamide with phosgene at 170°–180° (*v.* Basaroff, Ber. 1872, 5, 477), or by boiling it with phenyl carbonate (Cazeneuve, Compt. rend. 1899, 129, 834); by the action of phosphoryl chloride on a mixture of oxalic acid and carbamide, or on oxaluric acid (Grimaux, *ibid.* 1873, 77, 1548): or by distilling the monoureide of nitropyruvil $C_4H_3(NO_2)N_2O$ with bromine and water (Grimaux, *l.c.*; 1874, 79, 1478). Parabanic acid crystallises in flat, monoclinic prisms, soluble in 21·2 parts of water at 8°, and melts and sublimes at 100°. The *hydrate* $C_3H_2O_3N_2,H_2O$ or



$$CO<\begin{array}{l}NH\cdot C(OH)_2\\ \quad\;\;\cdot\\ NH\cdot CO\end{array}$$

is obtained when uric acid is oxidised with nitric acid (sp.gr. 1·3) at 35°–60°, it forms large compact crystals, soluble in 7·4 parts of water at 8°, becomes anhydrous at 150°–160°, and the dried substance recrystallises from water in anhydrous needles (Tollens and Wagner, Annalen, 1873, 166, 321; Tollens, Ber. 1872, 5, 801; Annalen, 1875, 175, 227). Parabanic acid has heat of combustion +212·7 Cal., heat of formation +139·2 Cal., heat of dissolution −5·1 Cal. at 20° (Matignon, Compt. rend. 1891, 113, 198); the dissociation constant for N/32 solution is $0{\cdot}75\times10^{-6}$ (Wood, Chem. Soc. Trans. 1906, 1835). In its physiological action parabanic acid resembles alloxan; it is eliminated in the urine partly unchanged and partly as oxalate (Pohl, Zeitsch. exper. Pathol. u. Ther. 1910, 8, 308); it acts on the central nervous system, producing first stimulation, then paralysis and finally kills in a state of torpor (Lusini, Chem. Zentr. 1895, ii. 311, 727, 838). Parabanic acid is a dibasic acid, the *ammonium*

$$C_3HO_3N_2(NH_4),$$

potassium $C_3HO_3N_2K$ and *sodium* $C_3HO_3N_2Na$ *salts*, prepared by adding alcoholic ammonia or potassium or sodium ethoxide to an alcoholic solution of the acid, are crystalline precipitates converted in aqueous solution into the corresponding salt of *oxaluric* acid

$$H_2N\cdot CO\cdot NH\cdot CO\cdot CO_2H;$$

the *mono-* $C_3HO_3N_2Ag,H_2O$, and *di-*

$$C_3O_3N_2Ag_2,H_2O$$

silver salts exist (Menschutkin, Annalen, 1874, 172, 73; Rudinskaia, J. Russ. Phys. Chem. Soc. 1885, 278); the *carbamide salt*

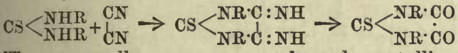
$$C_3H_2O_3N_2,CO(NH_2)_2$$

forms flat prisms (Hlasiwetz, J. pr. Chem. 1856, [i.] 69, 106).

Alkyl and aryl substituted parabanic acids have been prepared by the oxidation of certain purine derivatives, or more generally by the action of alcoholic silver nitrate on the corresponding thioparabanic acid. These compounds do not yield a precipitate with a cold solution of calcium chloride to which ammonia has been added, but on warming the mixture, calcium oxalate is precipitated (Andreasch, Ber. 1881, 14, 1447; 1898, 31, 137). *Methylparabanic acid* $C_3HMeO_3N_2$, by oxidising theobromine with chromic acid, or caffeine with bromine, forms transparent prisms, m.p. 149·5°; the *methylcarbamide salt* $C_4H_4O_3N_2,C_2H_6ON_2$ has m.p. 127°–128° (Maly and Hinteregger, Ber. 1881, 14, 723, 893; Monatsh. 1882, 3, 85; Fischer and

Frank, Ber. 1897, 30, 2609). *Ethylparabanic acid* $C_3HEtO_3N_2$, m.p. 45°; *allylparabanic acid*, m.p. 140°. *Dimethylparabanic acid, cholestrophan* $C_3Me_2O_3N_2$, obtained by oxidising caffeine with nitric acid (Stenhouse, Annalen, 1843, 45, 371; 46, 229), with chlorine water (Rochleder, *ibid.* 1850, 73, 57), or with bromine water, or by the action of methyl iodide on silver parabanate (Andreasch, Ber. 1898, 31, 138); melts at 145·5° and distils unchanged at 275°–277°, is soluble in 53·4 parts of water at 20° (Maly and Hinteregger, *l.c.*), and its heat of combustion is +539·1 Cal. (Matignon, Ann. Chim. Phys. [vi.] 28, 70). *Diethylparabanic acid* $C_3Et_2O_3N_2$, m.p. 46°; *methylethylparabanic acid* $C_3MeEtO_3N_2$, by oxidising ethyltheobromine, m.p. 44°; *methylallylparabanic acid* $C_7H_8O_3N_2$, m.p. 75°; *ethylallylparabanic acid* $C_8H_{10}O_3N_2$, m.p. 66°; *methylphenylparabanic acid* $C_{10}H_8O_3N_2$ m.p. 148°; *ethylphenylparabanic acid*, m.p. 97°. *Diphenylparabanic acid* $C_3(C_6H_5)_2O_3N_2$ by boiling dicyanodiphenylguanidine with hydrochloric acid, m.p. 204°; *di-p-tolylparabanic acid* $C_3(C_7H_7)_2O_3N_2$, m.p. 144°; *di-o-tolylparabanic acid.*

Thioparabanic acids are prepared by passing cyanogen gas into an alcoholic solution of the thiocarbamide and heating the resulting cyanides with hydrochloric acid.



$$\mathrm{CS}{<}\begin{matrix}\mathrm{NHR}\\ \mathrm{NHR}\end{matrix} + \begin{matrix}\mathrm{CN}\\ |\\ \mathrm{CN}\end{matrix} \rightarrow \mathrm{CS}{<}\begin{matrix}\mathrm{NR{\cdot}C:NH}\\ |\\ \mathrm{NR{\cdot}C:NH}\end{matrix} \rightarrow \mathrm{CS}{<}\begin{matrix}\mathrm{NR{\cdot}CO}\\ \mathrm{NR{\cdot}CO}\end{matrix}$$

They are yellow or orange-coloured crystalline compounds, and the thioparabanic acids corresponding with all the substituted parabanic acids described above have been prepared (Andreasch, Ber. 1881, 14, 1447; 1898, 31, 137).

M. A. W.

PARABISMUT *v.* SYNTHETIC DRUGS.

PARACONIC ACID *v.* LACTONES.

PARAFFIN. *Properties.*—Paraffin is a solid wax-like substance, colourless, tasteless, and odourless, composed of saturated hydrocarbons of the series C_nH_{2n+2}. In the market it is obtained with m.p. from 100°F. (38°C.) to over 135°F. (57°C.). The higher melting varieties are hard and tough at ordinary temperatures; all are plastic for some interval under their melting-points, and when fused are thin mobile liquids. Paraffin expands considerably in melting. With a wick it is easy to get it to burn with a clear white smokeless flame; but it does not burn readily in the mass. Its flashing-point is over 350°F. (177°C.).

The sp.gr. varies from 0·790 to 0·940 according to melting-point and origin. A sample with m.p. 38°C. had sp.gr. 0·8740 at 21°C., and the sp.gr. in the melted state, calculated to 21°C. was 0·795 (Beilby). The sp.heat is 0·694. It is a nonconductor of heat and electricity. It contains carbon about 85 p.c., hydrogen 15 p.c. It is insoluble in water, but soluble in ether, mineral spirit and carbon disulphide. It is characterised by indifference to most reagents, and can resist the action of many of the strongest chemicals even when heated.

Uses.—The harder paraffin is used in vast quantities for candle-making; the softer quality for miner's lamps, and household-, ship-, and hand-lamps; also for dipping the sticks of matches in place of the sulphur of long ago; and often gets the name of match or miner's paraffin. The peculiar properties of paraffin make it a useful material for many purposes, and as day by day it is getting more plentiful and of lower price its applications are extending. It is used for waterproofing cloth, leather, walls, cartridges, and wrapping paper; for coating the inside of vessels to prevent the wood giving a taste to the delicate substances in them, such as butter, mineral waters, beer, &c.; for coating metals to prevent rust and decay; for electrical insulation; for splints in surgery, as a medium for salves, for extracting perfume from flowers; for waxing thread, floors, &c., for heating-baths in laboratories, and numerous other purposes.

Production.—Paraffin is found native in various forms in the coal and other measures, *e.g.* as ozokerite (*q.v.*). A hundred years ago and more Uphall Parish and neighbourhood was lighted with ozokerite candles from Binny quarry, and these were the first paraffin candles to be used. Galician ozokerite is refined and sent into the market as ceresin. Paraffin was first produced in quantity from bituminous shale, and that is still an important source in Scotland, France, and Australia. In Germany it is obtained from the distillation of brown coal. It is now obtained from American, Galician, and other petroleums, but not from that of Baku. In shale oil and petroleum it is associated with liquid and gaseous members of the paraffin and other series of hydrocarbons. Scotch crude oil contains 11 p.c. of solid paraffin, brown coal tar 12 p.c., Galician petroleum 5 or 6 p.c., American 2 or 3 p.c., Upper Burmah and Assam sometimes 12 p.c. or more. For many years Scotland, with a yearly production of 20,000 tons was the principal producer in the world, but now America produces 100,000 tons, and Galicia now puts on the market over 60,000 tons per annum.

Distillation of bituminous shale for liquid products was tried in Scotland by Lord Dundonald as early as 1781, but the world was not ready for it. Previous to 1850 solid paraffin had been extracted in the laboratory from petroleums, wood-tar, and coal-tar, but throughout the world generally it was known only as a chemical curiosity. In France, however, manufacturing it had been attempted on a small scale as early as 1839, and candles proposed and patented in 1845. On the large successful manufacturing scale it was first produced in Scotland from torbanite, and this undertaking at once became well known and influenced the whole world. Later on oil shale was used.

Oil shale is at present worked for oil refining in Scotland, France, and Australia, and shale suitable for the purpose is found in Nova Scotia, New Brunswick, Servia, Spain, Tasmania, and many other places.

The methods of refining are the same for petroleum, brown coal, and shale oils, viz. fractional distillations alternated with treatments of oil of vitriol and of caustic soda; and the heavy oil when it contains solid paraffin, is cooled and pressed for its separation. A description of the Scotch manufacture is so far typical of all, but shale oil requires much more refining than petroleum. Crude petroleum is obtained directly by boring and pumping, whilst shale and brown coal have to be mined and retorted to get the crude oil. This extra expense is to some extent compensated for by the production of ammonium sulphate.

There is no hope of the petroleum wells lasting permanently, and the world's stock of it is being rapidly used up. The vast shale fields of the world will before long become of great interest and importance.

THE SHALE OIL INDUSTRY.

Locality.—At one time there were crude oil works scattered over all the British coal-fields. Now, however, all the oilworks existing in Britain are situated on a belt of the oil shale formation, 6–8 miles wide, stretching from the shores of the Firth of Forth at Abercorn and Dalmeny 16 miles southward to the east end of the Pentland range of hills at Cobbinshaw. Going due west from Edinburgh for 13 miles lands one in the middle of this tract. Besides this locality there is a regular strike of the shale seams in a narrow strip 10 miles to the east, where the seams lie much closer together. There were workings on it at the village of Pentland. This line is continued to the north side of the Forth and was worked at Burntisland.

The raw material used is a shale, which, while containing not more than 2 p.c. of true bitumen soluble in carbon disulphide, has much organic matter present capable of giving bituminous materials by destructive distillation. It is black or brownish in colour, fine in grain, free from grit, and with brown streak. It is tough, and good samples under the knife curl over in thin shavings, while poorer samples are more friable. Some good foreign shales have not this property of curling in thin shavings. It resists disintegration by weathering. Some shale is ‘plain,’ having the laminæ parallel with the stratification; other shale is ‘curly,’ side pressure while plastic having crushed it into wave-shaped, curled irregular masses, with black brightly-polished surfaces. The amount of shale distilled in Scotland in 1911 was 3,000,000 tons.

Products.—The crude oil, in amount about 70 million gallons or 273,500 tons per annum in Scotland, varies in proportion of products according to the nature of the shale and the retorting. The principal products are :—

1. Shale spirit or naphtha about 4 p.c. on the crude oil, sp.gr. 0·660–0·750, used as gasolene, motor spirit, solvent for india-rubber, burning in special lamps, &c. Water-white in colour.

2. Burning oil, 20–30 p.c., sp.gr. 0·785–0·830, used for lamps, and for internal combustion engines. Water-white or faint straw tint.

3. Intermediate oil, sp.gr. 0·840–0·865, 10–20 p.c. used for gas-making, gas-enriching, cleaning purposes, oil engine fuel, grease-making, and fuel for the navy.

4. Lubricating oil, sp.gr. 0·865–0·900, about 20 p.c., used for lubricating machinery. Clear yellow colour.

5. Solid paraffin, 10–12 p.c., *see* above.

6. Still coke, 3 p.c., used as a smokeless fuel for yachts, drawing-rooms, &c., and for electric candles, moulders' blacking, &c. Fixed carbon 95 p.c., ash 0·5 p.c., sulphur 0·4 p.c., volatile hydrocarbons 4 p.c.

7. Ammonium sulphate, about 60,000 tons a year, used as manure, especially for sugar beet growing, and largely exported.

8. The tars, 15 p.c., washed from the chemicals used in refining, are burned as fuel under the stills, sprayed with superheated steam.

9. Permanent gases are produced in the retorting and used as fuel for heating the retorts; and very rich pure gas is got in the refinery in distilling the crude and heavy oils to dryness and is used for illumination, and for fuel purposes under the stills.

The oil products are composed of the paraffin and olefine series of hydrocarbons with a small but definite admixture of naphthenes and benzenes. In the impurities extracted by the chemicals and the distillation are strong bases of the pyridine and quinoline series, phenols, cresols, pyrene, chrysene, and other hydrocarbons more dehydrogenated than the olefines; but the tars have not been thoroughly investigated.

History.—At Lyon Playfair's suggestion, James Young started, in 1848, a works in Derbyshire to refine petroleum from a spring found in connection with coal. The supply, some 300 gallons a day, soon threatened to stop, and Young, who supposed that this petroleum had been distilled by a natural process from the coal, set himself to create artificial petroleum by the distillation of coal at low temperatures. He experimented with many varieties, English and Scotch, and found that cannel or gas coals were suitable. He at last discovered the Torbanehill mineral near Bathgate, which proved exactly what was wanted. He took out his patent for low temperature distillation of coal in 1850, and the Bathgate works were in operation before the close of the year. Markets were soon created for lamp oil, which was the principal product, and also for lubricating oil and solid paraffin. Young introduced suitable lamps, and paraffin oil rapidly became the light of the people all over Britain. He called lamp oil paraffin oil, and paraffin oil, or simply paraffin, is the name yet commonly given in Britain to mineral oil for lighting purposes, whether of shale or petroleum origin. In America and on the Continent the name paraffin oil is applied to the heavy oil which is pressed directly from the solid paraffin. The manufacture proving a great success a good many works were erected throughout Britain during the run of Young's patent, and many were got ready to start on its expiry in 1864, and others were added afterwards. Factories were also started on the Continent, some of them getting the Torbanehill mineral exported to be distilled abroad. Many works were erected in America to work Young's patent and distil the native coals, and adopted his method of refining. Petroleum from oil springs began to be produced in quantity in Pennsylvania in 1859, and these coal refineries were in existence ready for its refining, and helped in the rapid development of the new industry. Coal oil was already well known in America, and petroleum lamp oil or kerosene is often yet called coal-oil in the States and Canada. In the sixties the exportation of American kerosene to the United Kingdom began and increased rapidly. The lamp oil fell in price from 2*s.* 6*d.* to 1*s.* 3*d.* per gallon, and many works had to stop. In 1871 there were 81 works, within two years only 30. The Americans at first exported only burning oil, and the Scotch modified their retorts to produce heavy oil and paraffin, and bought in American residuum to refine it. Soon the Americans took up these branches, and the United Kingdom was supplied with a superabundance of lubricating oil and solid paraffin, and their prices fell also. The ammonium sulphate, a by-product, became the saving of the industry, and the retorts were so modified that its production was doubled or trebled. About 1880 the supply of Peruvian guano, on which farmers had depended for their supply of combined nitrogen, now began to fail, and as a result the price of sulphate rose to £24 a ton, and the number of works was increased. But by 1890 sodium nitrate was imported in such quantities that the price of ammonium sulphate fell to £8 a ton, while burning oil brought only 6*d.* a gallon; and again there was collapse. The Russian petroleum industry had developed rapidly after 1873, and through time was competing in the English market for lamp and lubricating oils. Later on came competition from Galicia, Roumania, and the East Indies. The Scottish Industry has thus had many vicissitudes, times of success with expansion alternating with depression and collapse. When bad times came the weaker concerns ceased to exist, but the stronger ones enlarged their works to cheapen production by the many economies that enlarged output makes possible. In the sixty years of the existence of the industry 120 works have dropped out of existence causing the loss of several millions of capital, yet the yearly production has not declined but rather increased. There are now only seven companies in all, viz. four with refineries, and three which produce only crude oil and ammonium sulphate. In spite of the increased production of combined nitrogen from many new sources such as iron smelting, mondgas, coal coking, and electrical utilisation of atmospheric nitrogen, the demand of farmers all the world over has increased so that the price of ammonium sulphate has remained for a series of years from about £12 to £14 a ton. Shales that not long ago would have been rejected as rubbish are now most valuable on account of the large yield of ammonia, and the exhaustion of the shale supply is indefinitely postponed. Recent enlargement of the Scotch refineries, combined with the usual foreign competition, accentuated by the price war between the two great foreign petroleum corporations, have lowered the price of the oil and paraffin products, and the present outlook is discouraging. Further economies are necessary, and the combination of all the companies into one organisation, particularly in the selling department, suggests itself as possible.

The continued existence of this home industry has without doubt kept the light of the people at one-half the price of what it would otherwise have been, and a great deal cheaper than it is at the very gates of many American refineries.

Materials that have been used.—Young started the Bathgate works to distil the Torbanehill mineral (torbanite), called also boghead coal. It yielded 100–130 gallons of crude oil. Volatile matters, 65 p.c., ash 22 p.c. It was a rich shale rather than a coal. The residue left from retorting was not a coke as with coal, but was in thin layers like spent shale, and the crude oil was lighter, viz. sp.gr. 0·9, instead of 1·0 as with coal. It was getting exhausted and too expensive within a dozen years, and shales were used instead, and also some parrot coal. The shales at first tried yielded 45–30 gallons a ton, and those now in use give from 30 to 20 gallons. A 30 gallon shale has about 25 p.c. volatile matter and 75 p.c. fixed, of which 5 p.c. is carbon. The shale or parrot coals from the coal measures produced generally a crude oil having a higher sp.gr., more loss in refining, a thinner lubricating oil, and less solid paraffin than the shales of the shale measures.

Geology. The position of the shale measures in Scotland may be seen from the following statement in which the series are arranged in descending order:—

Carboniferous System
- Coal measures proper.
- Millstone grit.
- Carboniferous limestone series.
- Calciferous sandstone series, in which are the true shale measures.

Old red sandstone.

The coal measures proper with their many seams of workable coal have seams of shale or bastard cannel coal which could be profitably distilled in the early bright years of the industry. Over many ordinary seams of coal there was found a foot or more of suitable material which was kept apart and distilled. It was found, for instance, in connection with the splint and Virtuewell coals, the Musselband ironstone, and Kiltongue coal, in the Coatbridge district. Seams from the true coal measures were worked for oil in Fife, Ayrshire, and Midlothian, as well as throughout the English coal-fields in Yorkshire, Lancashire, Cheshire, and Stafford, and in particular there was for some time a considerable Welsh shale oil manufacture at Leeswood in Flintshire. The position of the Torbanehill mineral itself was near the base of the coal measure not far above the millstone grit.

The carboniferous limestone series with its valuable limestone, coal, and ironstone contains seams of shale and parrot coal that were worked for oil in Lanarkshire and Fife.

But foreign competition and low prices caused complete stoppage many years ago of all oilworks in Britain except those of the true shale measures.

The calciferous sandstone series, in its upper division, sometimes 3000 feet thick, contains all the oil shales worked at the present time. The seams, about twenty in all, vary much in thickness and quality in the different districts and the intervening strata are also variable. The following is a generalised section to show the succession, &c. The gallons are the crude oil, and the lbs. the ammonium sulphate, per ton of shale, as obtained in the modern retorts. The thickness in feet.

Hurlet limestone and coal, a widely known position reckoned the top of the shale measures. Strata, 400 ft. blaes, ironstone ribs, blackband ironstone, &c. (containing an upper Raeburn Seam at S. Cobbinshaw 100 ft. above the next shale).

Raeburn shale, 3–6 ft., 40–55 gals., worked at West Calder and Tarbrax. Strata 190 ft., blaes, ironstone bands, &c.

Mungle shale, 2 ft., 35 gals., 30 lbs. Strata 130 ft., blaes, fireclay, ironstone bands, volcanic tuff.

Two feet coal, with a thin *shale* and ironstone band. Strata Houston marls, 230 ft., thick beds, massive, amorphous, unfossiliferous.

Addiewell grey shale, 2 ft., composed largely of entomostraca. Strata 60 ft., blaes, fireclay.

Houston coal, 4–6 ft. Lowest coal that has been worked to any extent in Scotland. Inferior, pyritous, and interbedded with blaes. Strata 150 ft., laminated sandstone, blaes, clayband ironstone.

Fell's shale, 3–7 ft. Principal shale of West Calder district, 26–40 gals., 30 lbs. Strata, Broxburn marl, 135–270 ft., limestone immediately under Fell's shale, 3–6 ft., marly clays, cement stone, no sandstone.

Broxburn grey shale, 6 ft., 23 gals., 35 lbs. Strata 5 ft.

Broxburn curly shale, 5½ ft., 26 gals., 38 lbs. Strata 6 ft.

Broxburn seam, 5–6 ft., 30–35 gals., 40 lbs. At Midcalder there are other two seams above these three Broxburn seams, and another 16 ft. below the Broxburn. Strata 400–500 ft. blaes and marl, then the Binny sandstone, then again blaes and marl.

Dunnet shale, 4–12 ft., 24–33 gals., 24 lbs. At Oakbank there is a *lower dunnet shale.* Strata 400–600 ft., sandstone, blaes, lime ribs.

Barracks shale. Very variable, sometimes 8 ft., and yielding 22 gals., but generally thinner and poorer.

Burdie house limestone. A well recognised position. Sometimes 64 ft. quarried. Strata 600 ft., blaes and thick sandstones.

Pumpherston shales, 5 of them, with about 12 ft. of blaes between each pair, respectively 8, 5, 6, 7, and 4 ft. thick, 16–20 gals., 50–70 lbs.

The lower division of the calciferous sandstone varies from a hundred to several thousand feet in thickness. Sandstones, non-bituminous shales, cement stones, &c., fill up the space until the upper old red sandstone is reached. The Wardie shales (11 gals., 20 lbs.) of this lower division would not pay to work under present circumstances.

The oil shale measures are very much troubled. They are contorted into great waves, sometimes even overlap, and the same seams come to the surface at many places. There are four great faults running E. or N.E. with displacement of 1000–1500 ft., and numerous small faults or branches to the large ones. There are dykes of igneous rock running through the measures for miles. There are numerous necks of igneous rock coming up through the other strata; and there are many great sheets of intrusive sill intercalated between the normal strata, sometimes 5 or 6 ft. thick for a long distance, but here and there thickening to a great depth; sometimes keeping the same position for a wide space, then suddenly going higher or lower. The intruded mass has often taken the position of a good shale, utterly destroying it, and occasionally retaining some of the products of distillation in calcite-lined cavities in the mass of the sill, as liquid petroleum, solid bitumen, or substance of intermediate consistency like vaseline. Certain sedimentary strata are charged with petroleum and brine. The surface of the country has been partially levelled down in later ages by glacier action, leaving hills with crag and tail where the neck of igneous rock came up.

The calciferous sandstone turns up in a broad band from the east to the west of Scotland, but only in this limited locality of the Lothians has there been the suitable circumstances for the rapid deposit and preservation of the organic material that gives value to the shale. This has been called *sapropel* on the Continent and *kerogen* in this country. It is composed partly of amorphous jelly and partly of microscopical algæ, spores, and other minute forms of life, that seem to have been deposited in a brackish lagoon where there was little circulation and aeration of the water, so that on falling to the bottom they were enclosed in the mud and so preserved from decay. There have been great volcanos in the neighbourhood active during the deposit of this formation which first may have stimulated the minute life by warmth and afterwards by eruption caused their sudden precipitation to the bottom and envelopment in the mud. Dust thrown out by volcanos has formed extensive tuff strata throughout the district. Earthquake or poisonous gases may have caused the sudden death of the fish of the fish beds; and the many thin deposits of chemical limestone may have obtained the heat for the decomposition and precipitation of the bicarbonate from the neighbouring volcanos.

The shales worked in France and Australia belong to the carboniferous or permo-carboniferous epoch. Vast deposits still unworked are found in Canada in the upper old red sandstone. The Kimmeridge shale of England belongs to the Upper Jurassic. Oil shale may be got through a great range of geological time.

Mining.—The working is much like coal, pillar and stall, and the pillars removed later. Coal-cutting machines are not used. More is done by blasting in shale mines than with coal, various explosives being used, but mostly gunpowder. Boring for the shots is now done at several places by electrical machinery, a hole being drilled in 5 minutes that takes 45 minutes by hand. Most of the haulage, pumping water, &c. is now generally done by electric power, raised by steam. Before sinking a mine or pit in a new neighbourhood it has to be well explored by boring as the seams vary much, and the vagaries of the intrusive sill cannot be foreseen. The workings vary from 0 to 1000 ft. in vertical depth, one pit reaching 1600 ft. A seam is often richer towards the outcrop and poorer as it increases in depth, but not always. There is fan draught as in coal pits. The ventilation has to be good to sweep away the smoke of the shot-firing. Fire damp gives little trouble so that naked lights are in general use.

The manufacture is carried out in two divisions: I. the crude works, and II. the refinery.

I. *The crude oil works* consists of shale-breaking machines, retorts, condensers, receivers, scrubbing towers to take ammonia and light naphtha from the permanent gases of the distillation, a tower oil still and ammonia house. The crude works is situated in the middle of the shale field so that much of the shale is tipped into the breaking machine direct from the miners' hutches. It is expensive to convey shale far underground, and so mines or pits are put down all over the field and the shale brought in railway waggons to be emptied by hydraulic machinery into the breaking machine. If shale lies 5 miles or more from the refinery a crude works is put up there and the crude oil sent to the refinery by rail in tank waggons.

The breaking machines consist of two strong-toothed cylinders between which the shale is broken into pieces about 4–6 in. square. One machine with cylinders 3 ft. diameter and 4½ ft. long puts through over 500 tons in a day of 8 hours. The cylinders are of cast iron 3¼ in. thick with malleable steel teeth 2⅛ in. diameter and projecting 4½ in. outside the cylinder. The teeth of the one cylinder fall between the teeth of the other, and the clearance is self-adjusting 0–1 in.

Retorting.—The broken shale falls into hutches on rails holding about 18 cwt., to be taken by endless rope up an incline to the top of the benches and emptied directly into the retort hoppers. The retort hoppers are often so large that filled by day there is sufficient supply for all night. After distillation and passing down through the retort the spent shale falls into a hopper below, which is emptied at intervals, by day and night into iron hutches to be conveyed by endless rope or chain to the top of the spent shale bing.

Retorts are arranged in two rows in benches of 44–66 retorts. The distillation is upwards, and along the top of the retorts on each side there is fixed the main to carry off the products of distillation. The exit from retort to main is 7 in. diameter and the main itself 30 in.

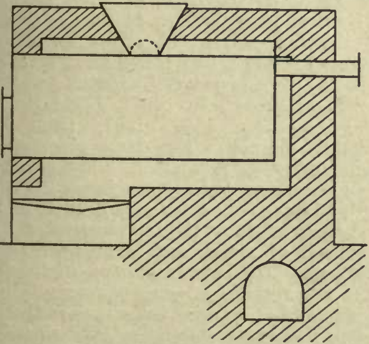


FIG. 1.

The first retort used by J. Young in 1850 was an imitation of the horizontal iron gas-retort of the time, but worked at as low a temperature as possible. Young soon adopted a vertical retort, but other works continued to use the horizontal type with improved arrangements until 1880 (Fig. 1).

The old vertical retort (Fig. 2), a cylinder about 1½ ft. in diameter and 10 ft. long, had a bell-hopper above for charging, and a water-lute below through which the spent shale was raked. It was charged at intervals of an hour, and a corresponding quantity of spent shale was withdrawn half an hour after the charging. Vertical retorts, improved in form and setting, oval in section, and lengthened to 15 ft., were in use in some works until after 1880. About 1860 steam had been introduced into the bottom of the retort. It moderated and transfused the heat, and swept the oil vapours rapidly out of the hot region, and the crude oil was improved in quantity and quality. These retorts were fired by coal, and the coal furnace heated three retorts on each side of it. They were often overheated, spoiling the oil and destroying the retort. Young recommended 600°–700°F., but old vertical retorts sometimes reached 1200°–1500°F. as measured by Siemens water pyrometer. The result was thus dependent on the care of the men.

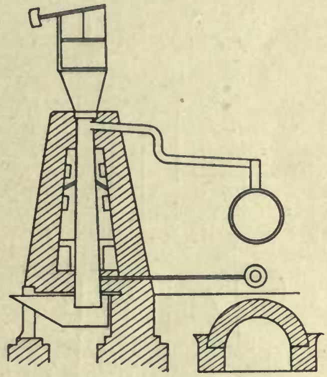


FIG. 2.

Many forms of retorts were patented. W. Young in 1867 tried a retort with gas-jacket around the metal retort. It was not a success, but it proved that a great improvement in the quality of the crude oil could be effected by gentle heating. The spent shale of the early retorts contained about 12 p.c. carbon, and a large proportion of the nitrogen. W. Young in 1872 attempted to utilise the spent shale for fuel with a gas lute between the products of combustion of the spent shale and the products of distillation. It required too much care in its management. N. M. Henderson in 1873 patented an arrangement by which the spent shale was dropped into a furnace below and served as fuel for the next charge (Fig. 3). This was an intermittent working retort. It held 18 cwt. shale, and was emptied and recharged every 16 hours. Four retorts were in an oven over one furnace and one was dropped every 4 hours. The fuel bill was greatly reduced, and the power to overheat was taken from the men and a greatly improved crude oil was the result. This retort was widely adopted for some time. The distillation was downwards.

The modern type of retort was the invention of George Beilby and William Young, experimenting at first independently and afterwards in partnership. The Young and Beilby retort, 1881, Fig. 4, was a continuous working one, vertical, with upward distillation. The upper part made of cast iron, the lower part of fire-brick, with a great hopper, on the top of all, common to four retorts. They were heated by gas fuel in flues around the retorts giving a long passage to the burning gases. The shale took 18 hours to pass down through the retort.

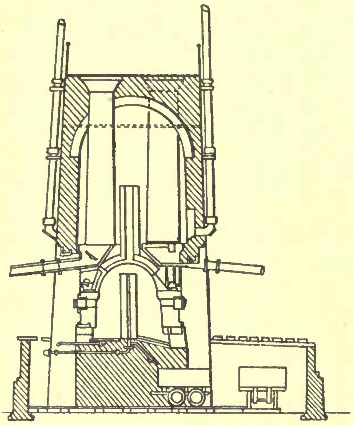


Fig. 3.

Steam introduced at the bottom was superheated at once by the hot spent shale. The temperature was not high enough for complete water gas, but the oxygen of the H_2O acted on the carbon of the spent shale to give CO and CO_2 in proportion according to the temperature, while the nascent hydrogen reacted on the nitrogen of the shale to produce NH_3. The lower or brick part of the retort is thus an ammonia and gas producer, and is worked at a high temperature, as high as can be ventured without fusing the ash. The permanent gas produced was over 10,000 cu. ft. against 2000 or 3000 of the earlier retorts, and the ammonia was doubled. The oil distillation took place in the iron part of the retort at a much lower temperature. The gases from the brick part were passed up through the fresh shale in the iron part, supplying heat, cushioning the large molecules against decomposition and sweeping the products rapidly out of the heat. The presence of ammonia increases the yield of solid paraffin (Tervet). The exit for the products of distillation was from the top of the great hopper. The crude oil condenses on the cold shale at the top to be redistilled as the shale slips further down, and it was claimed that a distillation of the crude oil in refining was saved. For extra fuel gas required, a coal gas-producer retort was placed here and there in the bench among the retorts, and the ammonia recovered; but such coal retorts were soon disused.

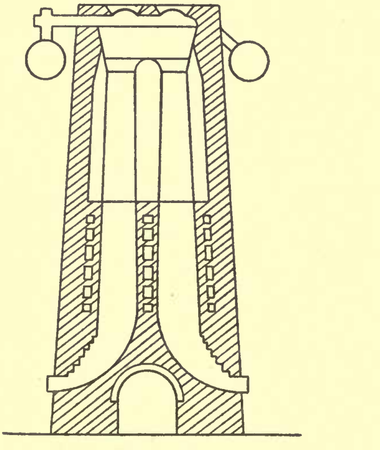


Fig. 4.

All the present retorts are of the Young and Beilby type. The form used by Young's company is very like the old Young and Beilby (Young and Fyfe, No. 13665, 1897; and No. 15238, 1899).

The retorts known by the names of Fyfe, Bryson, Crichton, and Henderson have this in common that they have a mechanical arrangement at the bottom of the retort, supporting the whole column of shale and spent shale, going constantly and regulating the amount put through. Bryson's, for instance, is a table with a revolving rake, Henderson's is two toothed rollers slowly revolving.

Henderson lengthened the retorts boldly and used Wilson's gas producer for supplementary fuel; but the larger size now used is so economical of heat that a 22-gallon shale requires no extra fuel of any kind, and has often excess of permanent gas so that after heating the retorts some is left to help in raising steam. The Henderson retort (Fig. 5) is now made in the metal part 14 ft. long, in the brick part 20 ft., and the total height to top of hopper is 63 ft. The section is oblong, 2 ft. 9 in. by 1 ft. 3 in. at the top of the metal part, and 4 ft. 8 in. by 1 ft. 10 in. at the bottom of the brick part. Each retort puts through 4½ tons in 24 hours, and the shale is in the retort for 27 hours (Patents No. 6726, 1889; and No. 26647, 1901).

In the Bryson retort (patented by Bryson, Jones, and Fraser, No. 8371, 1894; No. 7113, 1895; and No. 4289, 1897) (Fig. 6) the section is circular. This form gives strength and longevity and it can stand a higher temperature of working than other forms. The iron part is 15 ft. and the brick part 17 ft. 10 in. long; the diameter 2 ft. at the top of metal, 2 ft 4 in. at bottom of metal, and 3 ft. at bottom of brick part. The bottom hoppers of the retorts of the two rows in a bench converge so that a single line of rails under the centre of the bench receives the spent shale from both sides into a hutch, and reduces labour to a minimum.

These large modern retorts are never stopped for cleaning or any other purpose. The yield of ammonia is triple that of any retort previous to Young and Beilby's.

The temperatures of the flues around the Henderson retort, determined with the Féry radiation pyrometer, are, near the bottom of the brick part, 1000°C. (1832°F.), near the top of the brick part 850°C. (1562°F.), and in the oven of the metal part 670°C. (1238°F.). The temperatures used in the Bryson are much higher.

The products of retorting are crude oil, fuel gas, ammonia water, and spent shale. The great hills of spent shale are a conspicuous feature in the shale districts. The spent shale of the retorts previous to Henderson's 1873 patent contained 10–12 p.c. carbon and a large proportion of the sulphur. It gave trouble in the great heaps or bings by igniting spontaneously and burning quietly, giving off volumes of fumes containing SO_2 and H_2S. The well-exhausted spent shale of the present day is free from that nuisance. The original shale contains $1\frac{1}{2}$ p.c. sulphur.

The crude oil of the old vertical retorts was dark and tarry, sp.gr. 0·880–0·895. Henderson's 1873 retort produced a crude oil, sp.gr. 0·865–0·870, which yielded $2\frac{1}{2}$ p.c. more total products, all of improved quality, and contained $2\frac{1}{2}$ p.c. more solid paraffin. The Young and Beilby retort gave a slightly increased quantity of crude oil and of solid paraffin. The Bryson retorts are worked at a high temperature to produce a crude oil of 0·880 sp.gr. rich in paraffin but somewhat difficult to refine. The present Henderson retorts are worked at a mild temperature to give a crude oil of sp.gr. 0·868 and of good quality.

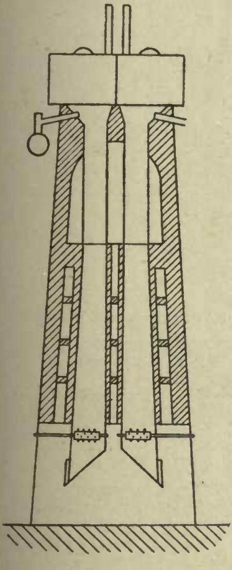


FIG. 5.

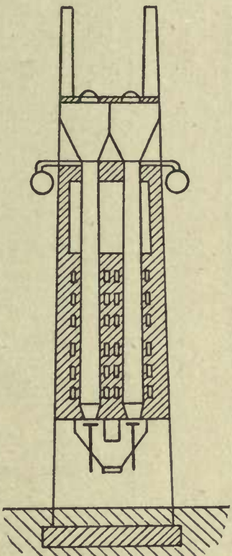


FIG. 6.

Retort condensers.—The vapours are led first through a tubular tower in the pipes of which the water for the steam boilers is heated; then through condensers. Many forms have been tried, but the universal arrangement now is great benches of 4-in. pipes, cooled by the atmosphere, and sometimes having a little water sprinkled over them. The pipes, 27 or 36 ft. high, are arranged vertically and fixed below in two rows into chests, two dozen pipes for the descending gases and the same number for the ascending, with arched connections at the top. There is about 100 lineal feet of this piping, or 100 cub. ft. of surface, for each ton of shale put through per day per retort. The water and oil condense separate from each other at once in a box called a separator and are run into their several receiving tanks. The gases pass from the condensers through scrubbing towers; one or two in series of water towers to catch the ammonia, and one or two of oil towers (oil sp.gr. 0·850) to catch the last of the condensable spirit. The gas is then caught by a fan which sucks the gases through the towers and condensers and pushes it forward to the retort flues where it is burned. The fan causes a suction equal to 6 in. of water, and this vacuum passes back to the retort, being equal to $\frac{1}{2}$–2 in. water at the retort exit. After burning in the flues of the retorts the products of combustion are passed off into the atmosphere by little chimneys at the top of the retorts, or are gathered into a common flue and taken to a tall chimney stalk. J. J. Coleman had a method of extracting gasolene from the permanent gases by cold and pressure. It was expensive, and has not been used for many years. The filling for the scrubbing towers now used is very various.

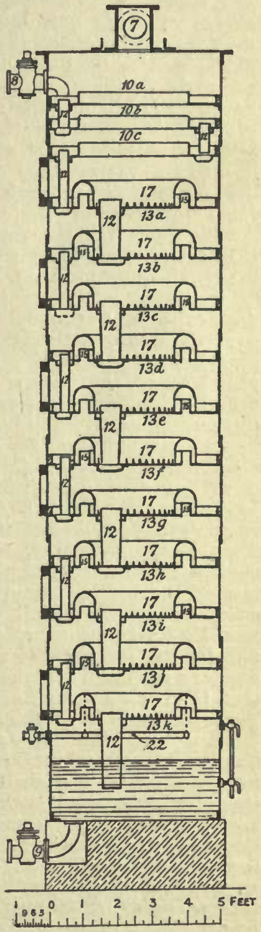


FIG. 7.

The ammonia water distillation is carried out in column-stills (Fig. 7), generally of circular section, and filled with a dozen or more trays. The feed water, after being heated in an exchanger by the spent ammonia water, travels down the column from tray to tray, while steam introduced at the bottom bubbles through each tray and liberates the free ammonia. Milk of lime is pumped into one of the trays near the bottom to release the fixed ammonia. The ammonia gases are led from the top of the still down to a 'cracker box' or saturator containing dilute sulphuric acid, and into which oil of vitriol is constantly run in a thin stream, and the ammonia is distributed from perforated lead pipes laid near the bottom. The bottom is sloped and the solid ammonium sulphate formed is swept into a well from which it is lifted by a steam injector and thrown into a conveying tub above, and the liquor lifted drains back into the cracker box, while the salt, after draining, is emptied into a bin. Here it drains or dries for a week before being ready for bagging for the market. The salt is now often centrifugaled direct from the saturator when it is ready for the market at once.

Acid water recovered from the acid tar of the oil refinery is saturated with ammonia in a somewhat similar manner. The saturation has to be complete, so as to separate the impurities. The excess of ammonia which escapes is caught in a vessel at a higher level containing the next charge of acid. The basic tar rises to the surface carrying with it the arsenic and the iron oxide, and is used as fuel. The solution of ammonium sulphate requires to be evaporated down. The oil of vitriol in the cracker box, previously described, requires diluting, and this solution is used. Any solution left is evaporated down in a vacuum pan something like those used for sugar, and the salt is sent into a centrifugal machine to dry it.

The steam from the cracker boxes containing CO_2 and some H_2S is passed into the shale retorts along with steam from the steam boilers.

The spent water has a strong smell and dark colour. It is pumped up and distributed over the hot spent shale on the bing where some is evaporated and the rest is filtered and passes off at the bottom of the heap, clear, colourless, and almost free from smell. Other dirty water is clarified in the same way.

In Germany there are a dozen brown coal distillation works, all in the Halle region. Over a million tons are distilled annually from 1300 retorts, producing 60,000 tons of crude oil, sp.gr. 0·850–0·910, and 7000 tons of paraffin wax. The burning oil, sp.gr. 0·825–0·830, requires special burners, and much is now used for internal combustion engines. The heavier oils, called yellow oil, red oil, and paraffin oil are used for internal combustion in Diesel engines, and for gas making, gas enriching, and liquid fuel, and not much for lubricating. The retorts used (Fig. 8) are vertical and of circular section. The outer wall is of firebrick surrounded by heating flues. The inner wall is formed of iron rings built together, louvre fashion, with openings between them. The shale moves down continuously in the space between the iron rings and the brick wall, and the central tube formed by the rings receives and carries off towards the condensers the products of distillation. The retorts vary in size. A cylinder 16½ ft. high and 6½ ft. wide puts through 20 tons of brown coal in 24 hours. The heating is done by coal, by gas, or by a mixture of both.

In France shale is distilled in three oilworks, one at Autun (Saône-et-Loire) and two at Bruxière-les-Mines (Allier). 160 retorts are in operation, distilling 150,000 tons yearly, and producing 2,440,000 gallons crude oil. The newer retorts are of the Young and Beilby type. The yield of crude oil is about 17 gallons to the ton, sp.gr. 0·912, and contains less than 3 p.c. paraffin. The crude oil is difficult to refine, and the burning oil is rather poor in quality. The gas oil is in large proportion. The lubricating oil, however, is of very good quality. The ammonium sulphate varies from 13 to 22 lbs. per ton. Two companies turn out coal from the shale mines and the other one works torbanite to sell to the gasworks; none work shale alone.

In Australia little shale is being distilled at the present time; but two large companies are erecting retorts and refineries in New South Wales, about 130 miles from Sydney. From the mines are to be got shale, torbanite, and common coal. The mining is mostly done on the longwall system, and no explosives used. The shale expands whenever the pressure is removed from it, and when undermined by the pick it soon falls down in pieces.

II. *The refinery* operations are distillations with fractionation into the several products; treatments with oil of vitriol and caustic soda; the recovery of the chemicals and the preparation of the tars for liquid fuel; cooling and refrigeration of the heavy oil, and filter-pressing to separate the liquid from the solid; and the sweating of the paraffin for its refining. Associated with the refinery is the despatch department with the oil-filling into barrels and railway tanks.

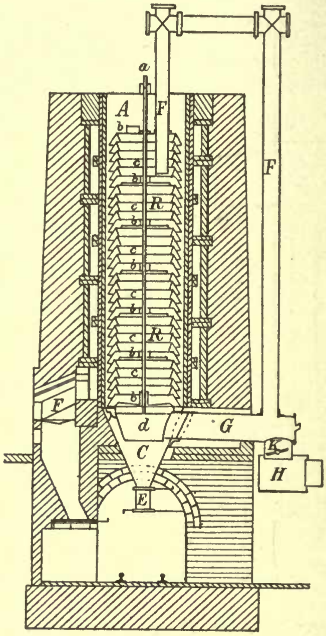


FIG. 8.

The stills are built in great benches with rows of high tanks built on roundels of circular brickwork, from which the oil flows by gravitation into the stills, and rows of tanks at a low level to receive the distillates. The system used by all the works is Henderson's continuous process (*see* Fig. 9) or a modification of it. There are cylindrical boiler-stills lying alongside each other, or sometimes waggon-shaped stills for the crude oil, connected together into a series through which the oil flows continuously, distilling off a fraction from each still, and venting finally into one of a group of residue stills. By means of a pipe within a pipe the oil flowing from the charging tank is heated by the vapours distilling from the second boiler of the series, and is landed hot inside the front of the first still. It travels from front to back, distilling off the lightest oil, which is condensed in a worm tank condenser. The oil not distilled is taken by a pipe and landed inside the front of the second still of the series, and it travels from front to back distilling off a second and heavier fraction; and on it goes through other boiler stills it may be, until at last the residue oil is passed into a still with pot-shaped cast-iron bottom. The residue still before being connected has a fire applied and steam passed through the still until all the air is blown out, so as to prevent explosion. Then the oil from the last boiler still is run in for some hours until the residue still is sufficiently loaded when the oil is shut off from this still and turned into another one. The disconnected still is then distilled to dryness and coked. There are safety valves on the residue stills in case the condenser should choke up with solid paraffin. At first two long troughs were suspended near the bottom of the cylindrical boiler stills to catch any coke or dirt in circulation; but these have been long disused. In all the distillations steam more or less superheated is passed into the distilling oil as it lowers the boiling-point and helps to carry the vapours over into the condensers. The first or crude oil distillation is meant to be to some extent a destructive one. If the chemical treatments with acid and soda were given direct to the crude oil the loss would be great; or if too much steam is used the oil distils over unchanged with the same result. So the steam is limited for the first distillation and also near the end of the second; but for the third distillation of the heavy or lubricating oil excess of steam is used: it helps to keep the viscosity of the oil high. In the lubricating oil distillation also dry caustic soda is put into the still, 2–5 lbs. per 100 gallons of oil. The condensers are coils of pipes laid in square iron tanks, carrying the vapours downwards, and cold water is passed into the bottom of the tank outside the pipes and overflows hot at the top, and the flow of water is regulated to suit the volatility and setting-point of the distillate. The condensed oil coming from the bottom of the condenser is passed through a U-bend of 8 in. depth on its way to the receiver, but before the bend a pipe rises vertically to take away the gases to prevent them being disagreeable or dangerous at the worm end. The gases used to pass into the atmosphere some yards up, now they are all caught and used for fuel or illumination. They are very rich and, from the second distillation especially, very pure. At coking of the residue stills and approaching the coking, torrents of permanent gas containing some light spirit are given off. Each works had its own method of catching the gases. In Henderson's system the gases are caught by a suction pump through a lute in a main common to a whole bench, the suction being automatically regulated so as not to suck air back through the bend of the oil exit.

In the first distillation many residue stills are required, in the later ones the distillation is mostly done in the boiler stills.

First distillation.—The crude oil is sometimes distilled from waggon-shaped boiler stills of this section (Fig. 9*a*), but oftener horizontal cylinders 7 ft. diameter by 19 ft. to 9 ft. by 30 ft. are used, the charge being 200–4000 gallons. The boiler stills are connected sometimes two in a series, sometimes three; or occasionally a central charging still supplies a boiler still, or even two, at each side. In all cases the tails run to residue stills. When two boilers are in a series, the distillate of the first is 0·760–0·770, of the second is 0·820–0·850, while the third in the series, the residue still runs from 0·850 or so when first connected to 0·930 or higher at the end of the distillation. At the end of the residue still distillation there comes over a yellow viscous product called still grease or chrysene which is used for grease making, or for liquid fuel.

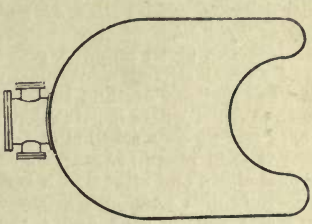


Fig. 9*a*.

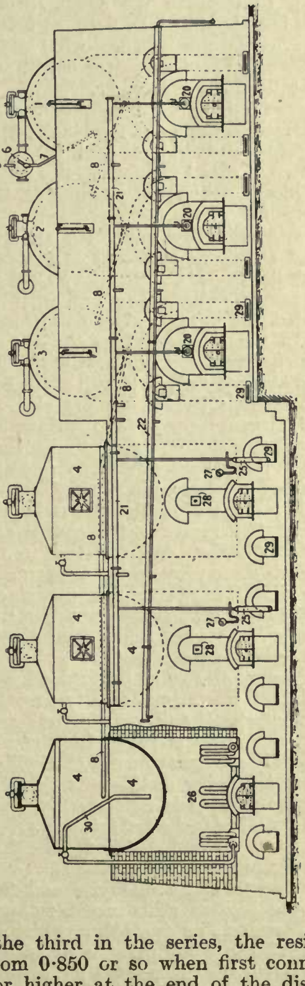


Fig. 9.

For an output of 50,000 gallons a day 4 or 5 boiler stills are required for the crude oil distillation with about 22 residue stills of 2000 gallons capacity each. The residue stills are connected for 4-6 hours each before disconnecting to distil to dryness. The still coke is copious and valuable.

The distillate of the first boiler still is kept apart as *green naphtha*, the distillates of the others, boiler stills and residue stills, are generally run together as *green oil*.

Treatments.—The green naphtha gets 2 p.c. oil of vitriol and is stirred mechanically, the black tar settled and run off, and the oil is run off into another vessel where it gets stirred with about 1 p.c. of caustic soda solution of 1·3 sp.gr. The naphtha is then ready for another distillation with steam alone, and after that it is colourless, but generally gets another treatment with acid, ¼ p.c., and caustic soda and a finishing distillation, to improve the smell. Distillates are sometimes separated as light as 0·660, but the usual gravities are between 0·700 and 0·750, 0·700–0·720 being sold as motor spirit, and the higher gravities for solvents, &c.

The green oil, sp.gr. 0·855, gets a 2 p.c. treatment with oil of vitriol, the black tar settled and separated and the oil run into another vessel, where it gets 1 p.c. of caustic soda solution, and after settling and running off the tar, it is ready for another distillation. All the stirrings, except for the naphthas, are done by compressed air. The green oil is stirred with the chemicals in large vessels, 30,000–40,000 gallons capacity, cylinders on end with cupped bottom into the centre of which the air is pressed. In the later stirrings the vessels are sometimes horizontal cylinders with the air distributed along the whole length of the bottom. After the stirrings the vessels are closed tight and the air pressure put on the surface to send the oil up into the charging tanks for next distillation. Sometimes the oil is pumped up.

The second or green oil distillation.—For a 50,000 gallons a day of crude oil, five boiler stills are required, two receiving the charge and the other three in series, and the tail to residue stills of which there may be ten or more.

1. The distillate of the two charging stills is about 0·800 sp.gr. It requires ¼ p.c. oil of vitriol and caustic soda, and a final distillation before the finishing treatment.

2. The second boiler in the series has sp.gr. about 0·815. It sometimes gets two treatments of ¼ p.c. oil of vitriol and caustic soda and two distillations before it is ready for the market, sometimes only one treatment and distillation.

3. The third boiler distillate is about 0·840, and after the paraffin is extracted is ready for market as gas oil or fuel oil of 0·850 sp.gr. Sometimes it is treated and distilled with finishing treatment for intermediate products.

4. The fourth boiler distillate and the distillate of the residue stills run together, give heavy oil containing paraffin, which, after separation of the solid paraffin as afterwards described, is *blue oil*. This gets 1 p.c. oil of vitriol and caustic soda, and is distilled again and fractionated into the various grades of lubricating oil, sp.grs. 0·865, 0·875, 0·885, and 0·895 when the paraffin is again extracted after chilling to a very low temperature. The blue oil distillation is sometimes carried out at once in 5000 gallon pot-stills (see Fig. 10) with dry caustic soda and excess of steam, sometimes it gets a concentration by passing through two boiler stills and the residue distilled in the pot stills with caustic soda.

The crude oil and green oil residue stills and often the lubricating oil stills are as shown in Fig. 11. Different works have somewhat different distilling arrangements and treatments, and even the same works is always changing somewhat to suit circumstances.

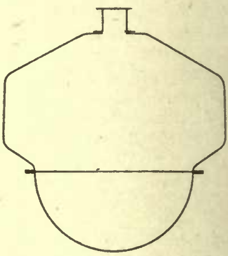


FIG. 10.

Finishing treatments.— Burning oil is treated with 1 p.c. oil of vitriol and weak caustic soda solution of about 1·04 sp.gr., and after settling with a little caustic soda solution of 1·33 sp.gr. is filtered through a filter press with paper instead of cloth. It is nearly water-white.

The heavy oils are treated with 2-4 p.c. oil of vitriol according to gravity, are settled all night, then finished with solution of sodium carbonate, as weak caustic darkens heavy oil, and after settling bright pumped to the filling tanks. It sometimes requires two or more days to settle the heaviest lubricating oils to brightness, and the following method has been tried for rapid clarifying. After the sodium carbonate tar is run off, open steam is blown in until boiling freely through the oil, then settled—and it settles rapidly at the high temperature—and the soda water is run off completely. Finally, air is blown through the hot oil until the oil is bright.

The soda tar of the finishing treatments is white.

The vitriol tar is washed with hot water, stirring the mixture with air and settling. This is done twice. The water seizes the sulphuric acid, and sets free the tarry bases. These are settled free from water, and burned under the boiler stills, &c., sprayed with superheated steam. The recovered acid is sent to the sulphate house to get saturated with ammonia as already described.

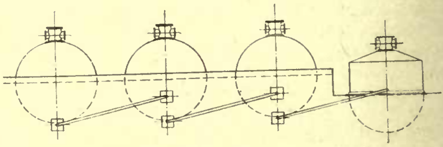


FIG. 11.

Separation of the solid paraffin.—One method is: The heavy oil containing solid paraffin is air-cooled in shallow tanks in covered sheds open to the wind, and in long cylinders with an inside stirring paddle. After this it is transferred to a cooler which is a tank divided into 6-in. wide spaces for the paraffin mass by 1-in. partitions containing circulating brine of calcium chloride from an ammonia freezing machine. The chilled part is constantly removed from the partition by a spring scraper. The mass lies in the cooler, in first cooling for 6 hours, in second cooling from 12–20 hours, according to sp.gr. After being broken up by a mechanical stirrer the mass is passed with considerable pressure through filter presses. The cakes of paraffin scale dropped from the filter-presses sometimes after melting up and recrystallising are sent direct to the sweating stoves without pressing in hydraulic plate presses. In other cases it is plate-pressed to separate the last of the oil.

Another method is: The mixture of heavy oil and paraffin is cooled in a tower by air current, then passed into a long vessel containing a stirrer where it is cooled by a cold-water jacket, afterwards passed into a cooler with stirrer where it is chilled by a jacket of the cold oil from the filter presses, then at last into a tube which may be vertical or horizontal, 17 in. diameter, with a scraper inside surrounded by a wider tube containing liquified ammonia gas which is evaporating rapidly into the vacuum of a suction pump. The oil and paraffin mass thus gets the final refrigeration and passes under high pressure from a pump direct to the filter-presses. The separated oil on its way out chills the oil coming in as stated and passes to a tank to be worked up for lubricating oil. The solid paraffin falling from the filter presses is broken up and conveyed by archimedian screw into the plate-press house, where it is pressed in cloths in hydraulic presses, and the last of the oil expelled. After this the paraffin is ready for sweating.

This direct application of the cold is more economical of the refrigerating power, and although gradual cooling is applied as much as possible, yet the sudden chill at the end causes some paraffin to separate in the amorphous state, and more filter presses are required than with the more gradual cooling with the brine. The brine-cooled paraffin is more crystalline, and therefore the liquid separates from the solid much more readily in the filter presses.

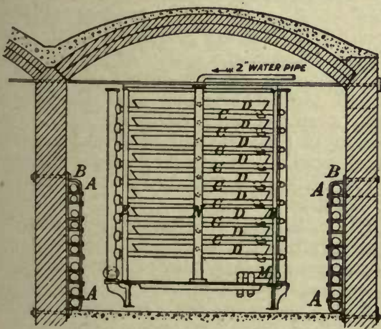


FIG. 12.

Paraffin is refined by a sweating process. Cakes of paraffin made by cooling and crystallising the melted solid are heated up gradually, when the oil and soft paraffin sweat out carrying the colouring matters along with them. N. M. Henderson's method is the only one used in Scotland, and it is in general use over all the world (see Fig. 12). In a great oblong chamber are built nine tiers of iron trays, in two stacks, making 18 trays in all. They are 6 in. deep, with a wire gauze shelf fixed 2 in. above the bottom. The trays are first filled with water up to the level of the wire-gauze shelf from a pipe at the end, which has a cock to each tray; then 2 or 3 in. of liquid paraffin are run on the top of the water. The great end doors of the chamber are open, and large apertures in the roof so that cooling takes place by natural draught. Sometimes artificial wind from a fan such as is used for mines is applied. When the paraffin is cooled and solidified, the water is run off from below, leaving the great cakes lying on the gauze shelf. By turning a large screw the trays are slightly tilted to help the draining. The doors are shut, and spent steam from pumps and engines is turned into heating pipes ranged up the sides of the apartment, and the temperature gradually rises. The oil and softest paraffin gradually drain out from the hard crystals, and the sweatings are fractionated into receivers according to setting or solidifying point and colour. When sufficiently sweated, live steam is turned on to pipes which support and separate the trays, and the refined wax is melted and run out into its own tank. Semi-refined wax is got by one sweating, and a repetition of the sweating produces refined wax; sweating in itself being sufficient. But sometimes the refining is finished by melting the semi-refined wax, mixing 33 p.c. of spirit of sp. gr. 0·735, cooling into cakes and pressing them, folded in cloth, in hydraulic plate presses. The expressed spirit carries away all colour. The smell of spirit is removed by steaming. Sweatings are themselves sweated at a lower temperature to get low melting-point waxes.

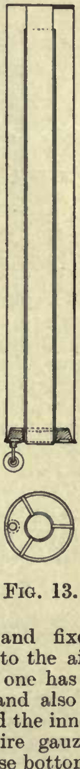


FIG. 13.

N. M. Henderson has adopted another method of sweating (see Fig. 13). The plant is cheaper, easier to erect, and more economical of space, and it gives a more thorough separation of oil from paraffin and a larger yield of finished wax. A cylinder 7 in. diameter is fixed concentrically within another of 17 in. diameter. Both are of thin iron, 9 ft. long, and fixed vertically. The centre one is open to the air, both at top and bottom. The outer one has a bottom with outlet pipe and cock, and also a false bottom a few inches up. Around the inner cylinder there are three plies of wire gauze. Water is run into the cell up to the false bottom, and the cell then filled with melted paraffin. After cooling in the same manner as the tray stoves, the water below is run off, and suction is applied to the bottom of the cells by a steam injector on the exit pipe common to a row of cells. The doors are shut and steam put on pipes laid below, and the sweatings find their way through passages formed at once by the heat among the layers of gauze. It has been proposed to expedite the operations by taking the chilled cakes falling from the filter presses, breaking them up and transferring at once to the cells, where the oil is sucked away before the cold paraffin reaches the atmospheric temperatures. The oil is free from dissolved paraffin. This saves the time and expense of melting up and recrystallising.

A double stove of 18 trays takes a charge of about 16 tons. Into the same space 144 cells are placed to hold more than twice the amount of paraffin.

In every case the final process is stirring the melted paraffin with 1 or 2 p.c. char (got from the old method of cyanide making) for 15 minutes, then at once, without settling, pumping the mixture first through a cloth filter-press, and then through one mounted with filter paper. These catch the char, and the wax is ready to run into cakes for the market, or direct into the candle-house tub. Long contact between char and wax is to be avoided for soon the melted wax begins to take up the colour again. The char retains a proportion of wax. This is recovered by a still like a Soxhlet apparatus on a large scale. If the paraffin is thoroughly washed out, the char, when retorted, is as good as at first; but ½ p.c. of paraffin left in spoils it.

Two of the refineries have candleworks. They supply some wax to other candlemakers, but they also buy much foreign wax to convert into candles besides the bulk of their own production.

Two of the refineries make oil of vitriol for their own use. All recover sulphuric acid from the vitriol tar and use it for making ammonium sulphate. They also recover a proportion of the soda they use.

There are rows of tanks to stock all grades of oil, especially vast tanks to store burning oil for winter use, and Admiralty fuel oil, and they are connected by pipes with taps in the filling houses to run the oils into barrels or railway tanks, or into drums, or tins for cases.

There are tradesmen's shops, wherever needed for mines or works, for smiths, fitters, joiners, plumbers, &c., and also saw-mills, steam-hammers, box-making machinery, and other necessaries and conveniences. About 10,000 men in all are employed.

The history of retorting, with many figures, is given by Beilby (J. Soc. Chem. Ind. 1897, 876); and in the same journal, 1897, are described the more modern retorts (Henderson, 984; Crichton, 988; and Bryson, 990). Refining is described (J. Soc. Chem. Ind. 1889, 100) with continuous distillation, &c.

PARAFFINIC ACID $C_{23}H_{47}COOH$, was obtained by Pouchet (Bull. Soc. chim. [ii.] 23, 111) by oxidising solid paraffin with nitric acid; m.p. 45°–47°.

PARAGUAY TEA or **YERBA DE MATÉ**, commonly known as *Maté*, or *Jesuits'* or *St. Bartholomew's tea*, consists of the dried leaves and shoots of *Ilex paraguensis* (A. St. Hil.) (an evergreen related to the holly) and other small trees of the same genus, growing in the mountain woods (known as Yerboles) of Southern Brazil, Argentina, and Paraguay. It is also grown in plantations and is now used as a common beverage by over 30 million of the inhabitants of the South American republics, but has not yet gained favour in Europe, although its use is increasing, especially in France.

The trees are usually about 15 feet high, but occasionally attain a height of over 30 feet. The leaves are from 4 to 6 inches long, lanceolate, with finely serrated margins, and slightly obtuse apex. The midrib and its branches (the so-called 'veins' or 'nerves') are very prominent on the under side of the leaf. As in ordinary tea, the 'veins' meet before reaching the margin, and the stomata, which are nearly circular, are very numerous.

In the preparation of maté, whole branches, together with the twigs and leaves, are cut down, dried and roasted on iron gratings over a wood fire until the proper flavour is developed, then beaten with sticks and the fragments of leaves and twigs roughly ground to a very coarse powder to form the *Yerba de Palos* of the Spaniards or *Caa-Guaza*. Other and superior grades known on the South American markets are *Caa-Cuys*, derived from the young leaf-buds, and *Caa-Miri*, which consists of the unroasted leaves freed from their tough fibrous veins and midribs.

The infusion is made by pouring boiling water directly into the cup containing a quantity of maté with a little sugar and sometimes lemon-juice, and is imbibed while very hot through a *bombilla* or tube perforated at the bottom or provided with wire gauze to prevent the passage of solid particles of the tea.

It is said to have valuable restorative qualities after violent or prolonged physical exercise, due no doubt in part to the presence of caffeine or theine which, however, is present in smaller proportion than in ordinary tea (*q.v.*), but its effect is narcotic rather than stimulative. It also possesses mildly aperient and diuretic properties.

The amount of caffeine found in maté by different observers varies greatly, but trustworthy analyses do not show much more than 1 p.c. The proportion of tannin is also small, being about 1·5 p.c. on an average, and in this respect maté is claimed to have an advantage over ordinary tea, as well as from the fact that it is less affected by variations in climatic conditions. The tannin is peculiar in character, as it does not precipitate potassio-tartrate of antimony nor tan leather. J. C.

PARALACTIC ACID *v.* LACTIC ACID.

PARALDEHYDE *v.* ALDEHYDE.

PARAMOL (*o*-amino-*m*-hydroxylbenzyl alcohol), $C_6H_3(OH)(CH_2OH)NH_2$, is a photographic developer, the action of which is intermediate between the developers of the phenol class and the amidophenol class (Eichengrün, Zeitsch. angew. Chem. 1901, 14, 1070). It is soluble in 12 times its weight of water, gives a bluish negative, and can be used for negatives, positives, and papers (Jahr, Brit. J. Photogr. 1902, 49, 32).

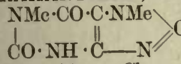
PARANEPHRIN *v.* SYNTHETIC DRUGS.

PARAPHENYLENE BLUE. This dye comes into commerce in three shades, which are designated respectively G, R, and B. They belong to a class of dyes obtained (according to Eng. Pat. 10134, of 1886) by heating paraphenylenediamine (or its homologues) with certain amino-azo- compounds—*e.g.* aminoazobenzene.

Paraphenylene blue R dissolves easily in water with a reddish-blue colour. Hydrochloric acid produces no change in the aqueous solution; but sodium hydroxide completely precipitates the dye in the form of a dark-violet precipitate. Tannic acid, in presence of sodium acetate, yields a blue precipitate, and the liquid is rendered colourless.

The boiling aqueous solution yields a black precipitate with potassium dichromate. The reactions shown by the other shades are similar. On wool, paraphenylene blue dyes direct in presence of a small quantity of acid. On cotton it is fixed by means of tannin and tartar emetic. The shades obtained resemble those produced by methylene blue. When chromed after dyeing the shades become considerably darker (J. Soc. Chem. Ind. 7, 561).

PARAROSOLIC ACID *v.* AURIN.

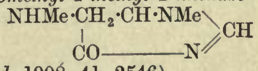
PARAXANTHINE, 1 : 7-*dimethyl*-2 : 6-*dioxypurine*  $\begin{array}{l}\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe} \\ | \qquad\qquad \| \\ \text{CO}\cdot\text{NH}\cdot\text{C}\text{——N}\end{array}\!\!>\!\text{CH}$, was discovered by Thudichum (Ann. Chem. Med. 1879, 1, 163; Compt. rend. 1888, 106, 1805), and independently by Salomon (Ber. 1883, 16, 195) in human urine, of which it is a normal constituent, and occurs to the extent of 1·3 grm. per 10,000 litres (Salomon, Virchow's Annalen, 1891, 125, 554; Salomon and Krüger, Zeitsch. physiol. Chem. 1898, 24, 364); and it is found together with other methylxanthines in the urine of dogs and rabbits that have been fed with caffeine (Krüger, Ber. 1899, 32, 2818, 3336).

Paraxanthine can be prepared synthetically from theobromine (3 : 7-dimethylxanthine) by the following series of reactions: theobromine is converted by the action of phosphoryl chloride into 2:6-dichloro-7-methylpurine; this on treatment with aqueous alkali and subsequent methylation yields 2-chloro-6-oxy-1 : 7-dimethylpurine, which is converted into paraxanthine by heating with hydrochloric acid (sp.gr. 1·19) at 125°–130° (Fischer, Ber. 1897, 30, 2400). Paraxanthine can also be prepared by reducing with hydrogen iodide and phosphonium iodide 8-chloroparaxanthine obtained from 1 : 7-dimethyluric acid by the action of phosphoryl chloride at 135°–140° (Fischer and Clemm, Ber. 1898, 31, 2622); or by the action of boiling water on 8-chloro-3-chloromethylparaxanthine obtained by heating caffeine with phosphoryl chloride and phosphorus pentachloride at 158°–162° (Fischer and Ach, *ibid.* 1906, 39, 423).

Paraxanthine crystallises in six-sided monoclinic plates, m.p. 298°–299° (corr.); in some preparations the crystals become cloudy or whitish at 110°, owing to loss of water of crystallisation, whilst others, isomorphous with them, remain bright (Salomon, *ibid.* 1883, 16, 195; Chem. Zentr. 1884, 490; Zeitsch. physiol. Chem. 1890, 15, 319). Paraxanthine is insoluble in alcohol or ether, dissolves in hydrochloric or nitric acid, or in ammonia; it is sparingly soluble in cold, more readily so in hot, water; at 40·1° 1000 c.c. of water or 1000 c.c. N/10 hydrochloric acid dissolves 1·06 and 1·17 grm. of paraxanthine respectively; the aqueous solution is neutral, and the basic dissociation constant is $3{\cdot}29 \times 10^{-14}$ (Wood, Chem. Soc. Trans. 1906, 89, 1842).

In its physiological action on frogs paraxanthine acts similarly to xanthine, theobromine, or caffeine, affecting the central nervous system and the muscles, and producing creeping movements, then the disappearance of all spontaneous activity and complete abolition of reflexes; the lethal dose is 0·15–0·2 per 1000 of the body weight. On mice the drug produces paresis of the hinder extremities, increase of reflex activity producing tetanus, the lethal dose is 2–4 times as large as for frogs (Salomon, Zeitsch. physiol. Chem. 1889, 13, 187). Paraxanthine acts as a diuretic when administered to rabbits (Ach, Chem. Zentr. 1900, ii. 688), and is excreted partly unchanged and partly as 1-methylxanthine (Krüger and Schmidt, Ber. 1899, 32, 2677).

Salts. (1) *With bases: sodium salt* $C_7H_7O_2N_4Na_3,4H_2O$, sparingly soluble crystalline compound, melts above 300°; the corresponding *potassium salt* has a higher melting-point (Salomon, *ibid.* 1883, 16, 195). (2) *With acids:* the *hydrochloride* $C_7H_8O_2N_4{\cdot}HCl,H_2O$ forms rhombic plates, dissociates in aqueous solution and loses HCl and H_2O at 100° (Pommerehne, Arch. Pharm. 1898, 236, 105); the *picrate* forms a yellow crystalline precipitate, decomposing in aqueous solution; the *nitrate* is unstable. (3) *Double salts:* with *mercuric chloride*, colourless prisms, melting with partial decomposition; the *aurochloride* $C_7H_8O_2N_4,HAuCl_4,\frac{1}{2}H_2O$, orange-yellow needles, m.p. 227°–228°; the platinochloride $(C_7H_8N_4O_2)_2,H_2PtCl_6,H_2O$, orange crystals belonging to the anorthic system (Pommerehne, *l.c.*; Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 24, 364).

Derivatives. 8-*Chloroparaxanthine*, m.p. 295° (corr.), soluble in 170 parts of hot water, crystallises in prisms; the *sodium salt* is sparingly, the *potassium salt* more readily soluble (Fischer and Clemm, Ber. 1898, 31, 2622); it reacts with amines to form the corresponding amino compound, and the compounds with ammonia, mono- and di-methylamine and aniline are described (Boehringer and Sohne, D. R. P. 156901). *Deoxyparaxanthine* $C_7H_{10}ON_4,H_2O$, obtained by the electrolytic reduction of paraxanthine, decomposes at 250° (Tafel and Dodt, Ber. 1907, 40, 3752), and is readily hydrolysed on heating with hydrochloric acid forming 5-*methylaminomethyl*-1-*methyl*-4-*iminazolone hydrochloride*  $\begin{array}{l}\text{NHMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NMe} \\ \qquad\qquad\quad | \\ \qquad\qquad\text{CO}\text{————N}\end{array}\!\!>\!\text{CH}$ (Tafel and Mayer, *ibid.* 1908, 41, 2546).

M. A. W.

PARCHMENT. *Parchemin* (Fr.); *Pergament* (Ger.). This writing material has been known since the earliest times, but is now made in a manner very superior to that by which it was anciently prepared, as we may judge by inspection of the old vellum and parchment manuscripts. The art of making parchment consists in certain manipulations necessary to prepare the skins of animals of such thinness, flexibility, and firmness as may be required for the different uses to which this substance is applied. Though the skins of all animals may be converted into writing materials, only those of the sheep or the she-goat are used for parchment; those of calves, kids, and still-born lambs for vellum; those of the he-goat, she-goat, and wolves for drum-heads; and those of the ass for battledores. All these skins are treated in the same way, with slight variations, which need no particular detail.

They are first of all prepared by the leather-dresser. After they are taken out of the lime-pit, shaved, and well washed, they must be set to dry in such a way as to prevent their puckering and to render them easily worked. The small manufacturers make use of hoops for this purpose, but on the larger scale a *herse* or stout wooden frame is employed. This is formed of two uprights and two cross-bars solidly joined together by tenons and mortices so as to form a strong piece of carpentry, which is to be fixed against a wall. These four bars are perforated all over with a series of holes of such dimensions as to receive slightly-tapered boxwood pins truly turned, or even iron bolts. Each of these pins is transpierced with a hole like the pin of a violin, by means of which the strings employed in stretching the skin may be tightened. Above the *herse* a shelf is placed for receiving the tools which the workman needs to have always at hand. In order to stretch the skin upon the frame, larger or smaller skewers are employed, according as a greater or smaller piece of it is to be laid hold of. Six holes are made in a straight line to receive the larger, and four to receive the smaller skewers or pins. These small slits are made with a tool like a carpenter's chisel, and of the exact size to admit the skewer. The string round the skewer is affixed to one of the bolts in the frame, which are turned round by means of a key like that by which pianos and harps are tuned. The skewer is threaded through the skin in a state of tension.

Everything being thus prepared, and the skin being well softened, the workman stretches it powerfully by means of the skewers; he attaches the cords to the skewers, and fixes their ends to the iron pegs or pins. He then stretches the skin, first with his hand applied to the pins, and afterwards with the key. Great care must be taken that no wrinkles are formed. The skin is usually stretched more in length than in breadth, from the custom of the trade, though extension in breadth would be preferable, in order to reduce the thickness of the part opposite the backbone.

The workman now resorts to the fleshing tool. It is a semicircular, double-edged knife, made fast in a double wooden handle. Other forms of the fleshing-knife edge are also used. They are sharpened by a steel. The workman holds the tool in his two hands so as to place the edge perpendicularly to the skin, and, pressing it carefully from above downwards, removes the fleshy excrescences and lays them aside for making glue. He now turns round the *herse* upon the wall, in order to get access to the outside of the skin and to scrape it with the tool inverted, so as to run no risk of cutting the epidermis. He thus removes any adhering filth, and squeezes out some water. The skin must next be ground. For this purpose it is sprinkled upon the fleshy side with sifted chalk or slaked lime, and then rubbed in all directions with a piece of pumice-stone, 4 or 5 inches in area, previously flattened upon a sandstone. The lime soon gets moist from the water contained in the skin. The pumice-stone is then rubbed over the other side of the skin, but without chalk or lime. This operation is necessary only for the best parchment or vellum. The skin is now allowed to dry upon the frame, being carefully protected from sunshine and from frost. In the arid weather of summer a moist cloth needs to be applied to it from time to time, to prevent its drying too suddenly, immediately after which the skewers require to be tightened.

When it is perfectly dry, the white colour is to be removed by rubbing it with the woolly side of a lambskin. But great care must be taken not to fray the surface—a circumstance of which some manufacturers are so much afraid as not to use either chalk or lime in the polishing. Should any grease be detected upon it, it must be removed by steeping it in a lime-pit for 10 days, then stretching it anew upon the *herse*, after which it is transferred to the *scraper*.

This workman employs here an edge tool of the same shape as the fleshing-knife, but larger and sharper. He mounts the skin upon a frame like the *herse* above described; but he extends it merely with cords, without skewers or pins, and supports it generally upon a piece of raw calfskin strongly stretched. The tail of the skin being placed towards the bottom of the frame, the workman first pares off with a sharp knife any considerable roughnesses, and then scrapes the outside surface obliquely downwards with the proper tools till it becomes perfectly smooth; the fleshy side needs no such operation; and indeed, were both sides scraped, the skin would be apt to become too thin, the only object of the scraper being to equalise its thickness. Whatever irregularities remain may be removed with a piece of the finest pumice-stone well flattened beforehand upon a fine sandstone. This process is performed by laying the rough parchment upon an oblong plank of wood in the form of a stool, the plank being covered with a piece of soft parchment stuffed with wool, to form an elastic cushion for the grinding operation. It is merely the outside surface that requires to be pumiced. The celebrated Strasburg vellum is prepared with remarkably fine pumice-stone. If any small holes happen to be made in the parchment they must be neatly patched by cutting their edges thin and pasting on small pieces with gum-water.

Another method of finishing the skin is to subject it, after a final scalding, to a bath of lime-water, and then powder it on both sides with French chalk, the excess of which is brushed off when dry. The skin is afterwards wiped over with a wet sponge and, when again dry, is rubbed over with a piece of flannel (Brand, Eng. Pat. 11693, 1893). Treatment with a bath of alum solution is said to prevent the ink soaking in and to make the parchment easier to use (Brand, *ibid.* 14384, 1894).

Parchment is coloured green only. The following is the process. In 500 parts of rain-water boil 8 of cream-of-tartar and 30 of crystallised verdigris; when this solution is cold pour into it 4 parts of nitric acid. Moisten the parchment with a brush, and then apply the above liquid evenly over its surface. Lastly, the necessary lustre may be given with white-of-eggs or mucilage of gum arabic (Ure).

PARCHMENT PAPER (*vegetable parchment*) is a modified form of paper, resembling parchment, produced by the action of sulphuric acid, zinc chloride solution or cuprammonium solutions on ordinary paper.

Manufacture by the sulphuric acid process.—The sulphuric acid used should have a density of 59°–60°B., and may be prepared by mixing 1 vol. of water with 2 vols. of ordinary strong sulphuric acid of 66°B. It is important that the temperature should not exceed 16°C. (Lotter, J. Soc. Chem. Ind. 1895, 58). The paper may contain linen or cotton fibres, or both, but regard must be had to the fact that linen is not parchmentised as quickly as cotton. The hardness of the original paper also affects the product in that a more porous paper absorbs the acid more readily and is more completely parchmentised and, therefore, more transparent. Because it is important for the acid to penetrate the fibre thick papers cannot be parchmentised, and thick vegetable parchment is made by pressing together two, three, or more sheets of thinner paper as they leave the acid bath. After they have been washed and dried it is found that they have become perfectly united.

In the hand process the operator, wearing rubber gloves, dips the sheets of paper into the acid bath for the requisite time (2–15 seconds, according to the nature of the paper and of the product desired), and then throws them into a bath of water, from which they are passed through other wash-waters, one of which contains a small proportion of ammonia. After a final wash the sheets are dried under pressure.

In the continuous process, a band of paper passes from a roll and under glass or lead rollers in the stoneware or lead tank containing the acid at such a rate that it is immersed for the time that previous experiment has shown to be necessary for its conversion into parchment. As it leaves the bath, it passes between rubber rollers, by which the excess of acid is removed and returned to the bath, and then goes through various washing tanks, one of which contains a dilute solution of ammonia. The washing is made more complete by spraying the paper with water (*see* Arnold, Eng. Pat. 8130, 1885; J. Soc. Chem. Ind. 1885, 609). After washing, the parchment is dried by passage over heated, felt-covered rollers, and is finally calendered in the same way as ordinary papers (J. Soc. Chem. Ind. 1894, 414; *see* also Wilbaux, Eng. Pat. 17268, 1890; J. Soc. Chem. Ind. 1891, 566).

Parchment paper is sometimes rather brittle when dry, and this is overcome by impregnating it with hygroscopic substances like calcium and magnesium chlorides and glycerol (Eichorn, Eng. Pat. 5610, 1885; J. Soc. Chem. Ind. 1885, 551). Robertson has patented a continuous process in which the paper, before drying, passes through a bath of glycerol (Eng. Pat. 8473, 1892; J. Soc. Chem. Ind. 1892, 935).

Vegetable parchment may be made white and opaque and repellent to water by adding to the acid-bath white opaque pigments, *e.g.* barium sulphate, and water-repellent substances, like mineral oils (Sachsenröder, Fr. Pat. 362463, 1906; J. Soc. Chem. Ind. 1906, 713).

Manufacture by zinc chloride and cuprammonium methods. The preparation of parchment-paper by the action of a very strong solution of zinc chloride upon ordinary paper differs little from the above method, except that a longer time is required for the action, and the alkali bath is omitted from the washing.

Cuprammonium solutions (*v.* Copper) gelatinise paper in a similar way and when the product is dried by steam-heat it is green, owing to the presence in it of copper.

Properties and uses.—The action of sulphuric acid in parchmenting paper is to convert the superficial layers of cellulose into a gelatinous mass which fills up the interstices between the fibres of the paper and renders it practically impervious to gases and liquids. During this change the paper shrinks 10–30 p.c. in area and up to 30 p.c. in thickness, and shows a corresponding increase in sp.gr. of 30–40 p.c. At the same time its strength is increased three- or fourfold and the product has about three-quarters the strength of animal parchment of the same thickness.

Good parchment paper is unaffected even by repeated soaking in boiling water and drying, and can thus be distinguished from various imitation parchment papers which are made by coating ordinary paper with size, albumin, blood serum, &c., with or without added colouring matter, and are at once disintegrated by hot water. In addition to being waterproof and gas-tight, it is unaffected by cold acids and by caustic alkalis; prolonged action of hot conc. hydrochloric acid, however, converts it into dextrin.

It is not liable to mould when damp and resists the attacks of insects, and thus possesses certain advantages over animal parchment. It takes dyes well.

It readily absorbs printers' ink and writing ink, and these cannot afterwards be erased without serious injury to the parchment. On this account it is much used for the preparation of important documents.

Vegetable parchment is also used for wrapping tobacco, &c., for luting the joints of stills, for covering jars containing preserves, &c., and for paper-bags for cooking and steaming food. It has been manufactured and used for electrical insulation (London and Bailey, Eng. Pat. 12711, 1895; *see* also L. E. Andés, The Treatment of Paper for Special Purposes).

PARIGENIN and **PARIGLIN** *v.* Sarsaparilla.

PARILLIN *v.* Glucosides.

PARILLINIC ACID *v.* Sarsaparilla.

PARIS BLUE. This term is occasionally applied to Prussian blue, and also to the products obtained by heating aniline with stannic chloride.

PARIS GREEN. An aceto-arsenite of copper used as a pigment, and occasionally as an insecticide on plants.

PARIS LAKE. *Carmine lake v.* Lakes.

PARIS RED. A variety of rouge employed for polishing.

PARIS WHITE. *Whiting v.* Paints.

PARIS YELLOW. *Normal lead chromate v.* Chromium.

PARSLEY. *Apiin*, the glucoside of apigenin, is found in the leaves, stem, and seeds of parsley (*Carum* [*Apium*] *Petroselinum* [Benth. and Hook]) (Rump, Bechner's Repert. f. Pharm. 1836, 6, 6; Braconnot, Ann. Chim. Phys. 1843 (iii.) 9, 250). Both authors obtained it as a gelatinous mass by extracting parsley seeds with boiling water, and considering the readiness with which it gelatinised, Braconnot included it among the members of the pectin class. Subsequently, Planta and Wallace assigned to it the formula $C_{24}H_{28}O_{13}$ (Annalen, 1850, 74, 262), and though by the action of boiling dilute acids a brown substance, $C_{24}H_{20}O_9$, was produced, it did not appear that apiin was a glucoside. On the other hand, Lindenhorn (Inaugural Dissert. Wurzburg, 1867), who obtained this substance in a crystalline condition, found that by the action of dilute acids it was decomposed into glucose and apigenin, and that the reaction probably proceeded as follows

$$C_{12}H_{14}O_7+H_2O=C_6H_4O_2+C_6H_{12}O_6.$$

Von Gerichten (Ber. 1876, 9, 1124), who found for apiin and apigenin numbers identical with those given by Lindenhorn, showed that on fusion with alkali apiin gave *phloroglucinol* and an acid not closely examined, but which, by the further action of the alkali, gave *protocatechuic acid* besides some *oxalic*, *formic*, and *para- hydroxybenzoic acids.* As a result of his investigation, von Gerichten considered the most probable formula for apigenin to be $C_{15}H_{10}O_5$, and that the decomposition of the glucoside apiin with acids might be represented as follows—

$$C_{27}H_{32}O_{16}+H_2O=2C_6H_{12}O_6+C_{15}H_{10}O_5.$$

In a later communication (Annalen, 318, 124), he adopted the formula

$$C_{26}H_{28}O_{14}\cdot H_2O,$$

and found that on hydrolysing apiin with ½ p.c. sulphuric acid it is converted into *apiose* and *a-glucose apigenin*

$$C_{26}H_{28}O_{14}+H_2O=\underset{\text{Apiose.}}{C_5H_{10}O_5}+\underset{\alpha\text{-glucose apigenin.}}{C_6H_{11}O_6\cdot C_{15}H_9O_4}.$$

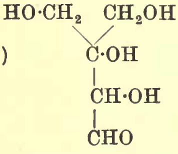
By the prolonged action of the acid, the latter compound gives apigenin and glucose

$$C_6H_{11}O_6\cdot C_{15}H_9O_4+H_2O=C_6H_{12}O_6+C_{15}H_{10}O_5.$$

Apiin therefore contains a disaccharose nucleus which on hydrolysis yields dextrose and apiose.

Apiose is an aldopentose of the formula (1) and on oxidation gives *apionic acid* (2)

(1)



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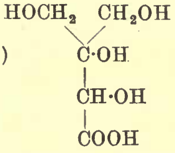


By the action of hydriodic acid and phosphorus apionic acid is reduced to *iso*-valeric acid.

When apiin is boiled with nitric acid in 60 p.c. acetic acid it is converted into the nitromonoglucoside, *nitroapigetrin* $C_{21}H_{21}O_{11}NO_2$, a yellow crystalline powder, m.p. 254°–255°, soluble in alkaline solutions with a yellow colour (Perkin, Chem. Soc. Trans. 1900, 416, 77).

Apiin consists of colourless needles, m.p. 228°, easily soluble in hot water and alcohol. From these solutions it separates on cooling in the gelatinous condition.

Whereas apiin can be most readily obtained in a pure condition from the seeds of parsley, it has been shown by von Gerichten that the stem and leaves of this plant contain in addition a glucoside of a *luteolin monomethylether.* By fusion with alkali, pure apigenin gives phloroglucinol and p-*hydroxybenzoic acid* (Ber. 1900, 33, 2334). The previous isolation of *protocatechuic acid*, according to this method by von Gerichten, and Perkin (Chem. Soc. Trans. 1897, 71, 805) was due to its contamination with a trace of the luteolin derivative.

In order to prepare apigenin, Perkin (*l.c.*) digests 30 grams of apiin for 20 hours with 3 litres of hydrochloric acid (sp.gr. 1·04). The crude colouring matter is extracted with boiling alcohol, and the extract treated with alcoholic lead acetate solution, drop by drop, until the supernatant liquid becomes colourless. The lead precipitate is then removed, and the filtrate after treatment with a few drops of acetic acid is evaporated to a small bulk. By addition of a little boiling water and gentle evaporation, the apigenin separates in a crystalline condition.

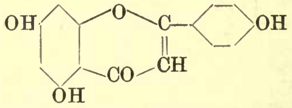
Should the substance be contaminated with luteolin monomethylether, it is digested for 2 hours with boiling hydriodic acid (sp.gr. 1·96) and the product crystallised from alcohol. The more soluble luteolin thus formed remains in solution (Czajkowski, v. Kostanecki and Tambor, Ber. 1900, 33, 1996).

Apigenin thus prepared crystallises in almost colourless leaflets, m.p. 343°, and dissolves in alkaline solutions with a yellow colouration. By means of acetic anhydride *triacetyl apigenin*, colourless needles, m.p. 181°–182°, is produced (C., K. and T.), but when methylated by means of methyl iodide, only a *dimethylether*

$$C_{15}H_8O_3(OCH_3)_2,$$

pale yellow needles, m.p. 171°–172° (Perkin, *l.c.*), can be prepared. On acetylation this yields *acetylapigenin dimethylether*, colourless needles, m.p. 195°–196° (P.), and by means of alcoholic potash is transformed into a yellow potassium salt which is decomposed by washing with water. When hydrolysed with alcoholic potash, apigenin dimethylether yields *anisic acid* and a syrupy phenolic substance which probably contains *phloroglucinol monomethylether.*

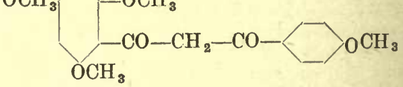
If apigenin is digested with 50 p.c. potassium hydroxide solution, it is hydrolysed with formation of p-*hydroxyacetophenone* and phloroglucinol (Perkin, *l.c.*). From the result of his investigation, Perkin assigned to apigenin the constitution of an *hydroxychrysin*, or 1 : 3 : 4′ : *trihydroxyflavone*



Somewhat later, Czajkowski, v. Kostanecki and Tambor (*l.c.*) synthesised apigenin by a series of reactions similar to those employed for the preparation of chrysin (Emilewicz, v. Kostanecki and Tambor, Ber. 32, 2448).

Phloracetophenone trimethylether condensed with *ethyl anisate* in the presence of sodium gives *tetramethoxybenzoylacetophenone* (1), and this on boiling with hydriodic acid is converted into apigenin (2).

(1)



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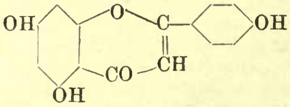


The following derivatives of apigenin have been prepared.

Apigenin diethylether, $C_{15}H_8O_3(OC_2H_5)_2$, yellow needles, m.p. 161°–162° (P.), 163°–164° (C., K. and T.); *acetylapigenin diethylether*

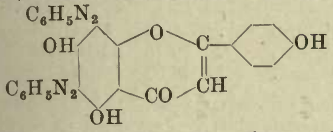
$$C_{15}H_7O_3(OC_2H_5)_2\cdot C_2H_3O$$

colourless needles, m.p. 151°–152° (P.). 148°–149·5° (C., K. and T.); *tribenzoylapigenin* $C_{15}H_7O_5(C_7H_5O)_3$, colourless needles, m.p. 210°–212° (P.); *dibromapigenin* $C_{15}H_8Br_2O_5$, pale yellow needles; *mononitroapigenin*

$$C_{15}H_9O_5{\cdot}NO_2,$$

orange yellow prismatic needles; *trinitroapigenin* $C_{15}H_7O_5(NO_2)_3$, minute yellow needles; and *tetranitroapigenin* $C_{15}H_6O_5(NO_2)_4$, almost colourless needles, m.p. 243°–244° (decomp.).

Disazobenzene apigenin crystallises in red needles (Perkin, *l.c.*), m.p. 290°–292° (decomp.)



and with acetic anhydride gives only the *monoacetyl-derivative* $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$, orange red needles which commence to decompose at 260° and melt at about 277°–280°.

Apigenin closely resembles chrysin in its tinctorial properties, although it is a somewhat stronger dyestuff. The shades it gives upon wool mordanted with aluminium, chromium, and iron are respectively pure yellow, weak yellow orange, and chocolate brown.

Apigenin is also present in weld (*Reseda luteola*) (Perkin and Horsfall, Chem. Soc. Trans. 1900, 77, 1314), and exists probably also in camomile flowers (Perkin) (private communication). A. G. P.

PARSLEY, OIL OF, *v.* Oils, essential.

PARSNIP, *Peucedanum satirum* (Benth. and Hook.). The tap root is used as a vegetable. König gives as the average composition—

Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash
83·2	1·4	0·4	2·3	8·1	3·6	1·0

It has also been used as a root crop for the feeding of horses, cows, and bullocks. The yield is from 12 to 24 tons per acre, and the material possesses higher feeding value than turnips, mangolds, or carrots (Guépin, Ann. Agron. 1900, 26, 476). The ash is rich in potash (42 p.c.). H. I.

PARTING. The separation of gold and silver by means of nitric acid, *v* Assaying.

PARTINIUM. An alloy of aluminium and tungsten used in automobile construction.

PASTES *v.* Gems, imitation.

PATCHOULI CAMPHOR *v.* Camphors; also Oils, essential.

PATCHOULI OIL *v.* Oils, essential.

PATENT LEATHER VARNISH *v.* Varnish.

PATENT PHOSPHINES *v.* Acridine dyestuffs.

PATERAITE *v.* Molybdenum.

PATINA. The green film which forms upon bronze and copper mouldings, and consisting of basic copper carbonate. On bronze statues it produces a pleasing effect owing to its colour, smoothness, and transparency, so that the bronze itself may be seen through it in places. The conditions which favour the formation of patina are a pure atmosphere, the presence of moisture in the air or in the earth where the articles may have lain buried, and a smooth surface. The finest examples of patina are found upon bronzes of ancient manufacture in which much tin and little zinc was used as alloy. The effect of a natural, and consequently slowly formed, coating of patina is frequently imitated artificially by wetting articles of bronze with dilute acids.

PATRONITE. A vanadium sulphide (VS_4 or V_2S_5+nS), forming a large deposit in the Quisque (or Minasragra) district, near Cerro de Pasco in Peru. It is amorphous and dull with a black or very dark greenish-black colour, and somewhat resembles asphaltum in appearance. Analyses show 15 to 24·8 p.c. of vanadium with combined sulphur and various impurities (silica, alumina, free sulphur, carbonaceous matter, &c.). Sp.gr. 2·65–2·71. Banded with vanadiferous asphaltum, quisqueite (*q.v.*), and a coke-like material, it forms a large vein or lenticular mass in red shales of Cretaceous age which are penetrated by dykes of igneous rock. This deposit has been extensively mined; the material is roasted to drive off volatile constituents, and the residue exported for the manufacture of vanadium steel. (*See* W. F. Hillebrand, Amer. J. Sci. 1907, xxiv, 141; D. F. Hewett, Trans. Amer. Inst. Mining Engin. 1910, xl (1909), 274) (*v.* Vanadium). L. J. S.

PAULLINITANNIC ACID *v.* Guarana.

PAVIIN *v.* Horse Chestnut.

PAWPAW, *Carica Papaya* (Linn.). The fruit is edible. According to Prinsen Geerligs (Chem. Zeit. 1897, 21, 719), the following figures give its average constitution:—

Average wt. of 1 fruit	Flesh	Rind	Seeds
600 grammes	65	10	25 p.c.

The flesh contains—glucose, 2·6 p.c.; fructose, 2·1 p.c.; cane sugar, 0·9 p.c.

Of more importance is the occurrence in the juice of the fruit, of an enzyme—*papayin* or *papain*—which resembles pepsin. In the West Indies this juice is collected by making incisions in the fruit while still on the tree, with a bone or wooden knife, and receiving the juice in earthen or glass vessels. The juice, which rapidly coagulates to a white curd, is very putrescible, and has therefore to be rapidly dried, either in the sun or by artificial heat, care being taken not to raise the temperature much above 35°–40° (*v.* Papain).

H. I.

PEA. The garden pea, *Pisum sativum* (Linn.), is a leguminous plant, growing in temperate climates. The seeds are used largely as human food in the green immature condition and also when ripe and dry.

The air-dried ripe seeds, on the average, contain (König)—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
13·6	23·4	1·9	52·7	5·6	2·8

Of the total nitrogen in peas, non-proteid nitrogen constitutes from 8 to 11·5 p.c. The proteids have been investigated by Osborne and Campbell (J. Amer. Chem. Soc. 1896, 18, 583; *ibid.* 1898, 20, 348 and 410), who find them to consist of *legumin* and *vicilin*, together amounting to about 10 p.c., *legumelin* about 2 p.c., and two other substances, *protoproteose* and *deuteroproteose*. Legumin is a globulin not coagulated at 100° and containing 17·75 p.c. nitrogen and 0·46 p.c. sulphur; vicilin is a similar substance, but coagulates at 95° and contains 17·15 p.c. nitrogen and only 0·1 to 0·2 p.c. sulphur;

legumelin is an albumin, coagulates below 80° and resembles the leucosin of wheat (Osborne and Harris, J. Biol. Chem. 1907, 3, 213). For description of the hydrolysis of these proteids, *v.* Osborne and Heyl J. Biol. Chem. 1908, 5, 187.

Choline and trigonelline have been found in peas (Schulze and Frankfurt, Ber. 1894, 27, 769).

The nitrogen-free extract contains about 68 p.c. of starch, 10·5 p.c. of dextrine, &c., and 4 p.c. of pentosans. The fat is a pale-yellow oil, containing much lecithin and some phytosterol.

Green peas—the unripe form in which the seeds are usually eaten as a vegetable, contain on the average—

Water	Protein	Fat	Sugar and other N-free subst.	Crude fibre	Ash
77·7	6·6	0·5	12·4	1·9	0·9

The nitrogenous matter consists largely of non-proteid bodies, 25–33 p.c. of the total nitrogen being in this form.

The ash of peas contains—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
41·8	1·0	5·0	8·0	0·9	36·4	3·5	0·9	1·5

Bottled and canned green peas are largely prepared, and in many cases the colour is rendered brighter by the use of copper compounds, added either by actual addition of some copper salt or by boiling the peas in a copper vessel. According to Tschirch, an insoluble phyllocyanate of copper, $Cu(C_{24}H_{27}N_2O_4)_2$ is produced in the tissues of the pea by such treatment; 50 milligrams of copper per kilogramme of peas is said to be sufficient to impart a permanent and adequate greenness to peas, and twice this amount is permitted by law in France and Italy (Wynter Blyth). Such addition of copper is illegal in England.

The field pea, *Pisum arvense*, is an important farm crop, the seed furnishing an excellent and richly nitrogenous food for fattening stock, while the power of collecting nitrogen from the air, which peas in common with other *leguminosæ* possess, serves to enrich the soil on which it is grown.

The following analyses by Kellner show the average composition of field peas :—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Green plant, flowering	84·6	4·0	0·5	5·1	4·5	1·4
Hay, cut in flower .	16·7	14·3	2·6	34·2	25·2	7·0
Straw, cut when ripe .	13·6	9·0	1·6	33·7	35·5	6·6
Seeds, air-dried . .	14·0	22·5	1·6	53·7	5·4	2·8
Husks . . .	12·0	7·3	1·2	31·9	44·7	2·9
Bran . . .	11·7	16·8	1·7	46·2	20·1	3·5
Feeding meal . .	13·5	23·4	2·0	51·0	7·0	3·1

H. I.

PEA IRON ORE *v.* Iron.

PEA-NUT, Earth-nut or **Ground-nut,** *Arachis hypogœa* (Linn.), the seed of a plant growing in warm climates. After flowering, the stalk bends over and enters the soil, where the seeds grow and ripen. The seeds are contained in paper-like pods, or husks, and there are usually two, though in some varieties four seeds in each pod.

The average composition of the shelled seed is given by König as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
7·5	27·5	44·5	15·7	2·4	2·5

The writer has found in samples of Transvaal pea-nuts considerably higher proportions of oil, *e.g.* the following three analyses may be quoted (A grown in the Transvaal from Virginian seed; B grown in the Transvaal from Spanish seed; C imported seed, variety 'Mammoth'):—

100 pods of A weighed 155·4 grammes and contained 169 kernels;

100 pods of B weighed 102·4 grammes and contained 170 kernels;

100 pods of C weighed 190·3 grammes and contained 288 kernels.

A consisted of 66 p.c. kernel, B of 76·4 p.c., and C of 71·7 p.c. kernel.

The kernels, on analysis, gave the following :—

	A	B	C
Moisture .	4·88	5·05	4·37 p.c.
Protein . .	30·13	31·19	24·82 ,,
Oil . . .	46·06	46·08	54·35 ,,

The seeds, after roasting, possess an agreeable nutty flavour, and are used to some extent as human food. They are of more importance as a source of oil (*v. Arachis oil*, Art. Oils, Fixed, and Fats), while the press cake left is a valuable cattle food containing, according to Kellner—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
9·8	44·5	9·2	23·8	5·2	7·5

Samples containing up to 50 p.c. protein are not uncommon, and, if the seeds are free from sand, the ash is lower than the figures given.

The 'vines,' after removal of the seed, may be used as hay for cattle. American analyses show them to contain—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
10·0	10·0	3·6	42·0	22·0	12·4

For a description of the cultivation and applications of the pea-nut or 'pindars' in Jamaica, *see* J. Imp. Inst. 1898, Dec. 341.

H. I.

PEACH, *Prunus Persica* (Stokes), a tree growing in warm climates, bearing a fruit which is valued for table purposes. Many varieties are known; they may be divided into two types—cling-stone and free-stone peaches, according to the character of the connection between the flesh and the stone or 'pit' of the fruit.

König gives as the average composition—

Water	Protein	Free acid	Invert sugar	Cane sugar	Other N-free ext.	Fibre	Ash
82·0	0·9	0·7	3·7	4·5	1·2	6·5	0·6

Under 'fibre' in the above figures is included the stone, which constitutes from 4·6 to 6·8 p.c. of the whole fruit. About 0·8 p.c. of pentosans is present. The peach kernel contains a fixed oil, amygdalin, and a proteid, *amandin* (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 609). For changes in composition during ripening, *v.* Bigelow and Gore (J. Amer. Chem. Soc. 1905, 27, 915).

The juice of peaches has a sp.gr. of about 1·05, contains 13 p.c. of total solids, including 2 p.c. invert sugar, 7 p.c. of cane sugar, and 0·6 p.c. free acid (as malic acid). It can readily be fermented, and is used as a source of alcohol—so-called peach brandy.

Peaches are often preserved by drying, or canning in syrup. American analyses of canned peaches show them to contain—

Water	Protein	Fat	N-free extract and fibre	Ash
88·1	0·7	0·1	10·8	0·3

H. I.

PEACH KERNEL, OIL OF, *v.* OILS, ESSENTIAL; *also* OILS, FIXED, AND FATS.

PEACH WOOD *v.* BRAZIL WOOD.

PEACOCK-COPPER ORE *v.* COPPER-PYRITES.

PEAR, *Pyrus communis* (Linn.). Many varieties are known. The average composition of the ripe fruit is given by König as—

Water	Protein	Free acid	Invert sugar	Cane sugar	Other N-free extract	Fibre and pips	Ash
83·8	0·4	0·2	7·1	1·5	3·4	2·8	0·3

A considerable quantity of pectin and pectous substances is present. Pear juice, like apple juice, readily ferments and yields an alcoholic liquid—perry—resembling cider. From this a brandy can be prepared (*v.* Windisch, Zeit. Spiritusind. 1905, 2887). Tannin is present, especially in the rind (Kehlhofer, Bied. Zentr. 1900, 29, 248). The rind also contains a wax melting at 68° (Seifert, Landw. Versuchs. Stat. 1894, 45, 29). The dried seeds of pears were examined by Huber (Landw. Versuchs. Stat. 1911, 75, 443), who found them to contain—

Fat	Sugar	Furfuroids	Crude fibre	Protein	Amides	Ash
25·0	5·4	6·7	9·0	5·4	0·2	3·8

The leaves of pear trees contain from 1·2 to 1·4 p.c. of a glucoside (m.p. 194°), which, on hydrolysis, yields quinol, and is probably identical with arbutin (Bourquelot and Fichtenholz, Compt. rend. 1910, 151, 81). The existence of quinol in the buds of peartrees was observed by Rivière and Bailhache (Compt. rend. 1904, 139, 81).

The ash of pears (whole fruit) was found by Wolff to contain—

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2
54·7	8·5	5·2	8·0	15·3	5·7	1·5

Pears are sometimes dried, but more generally preserved by canning. American analyses give the following:—

	Water	Protein	Fat	Total carbohydrates	Ash
Dried pears .	16·5	2·8	2·4	72·9	2·4
Canned pears	81·1	0·3	0·3	18·0	0·3

H. I.

PEARCEITE *v.* POLYBASITE.

PEARL ASH. A variety of potassium carbonate, *v.* POTASSIUM.

PEARL SINTER. A kind of opal found in the cavities of volcanic tufa.

PEARL SPAR *v.* DOLOMITE.

PEARL WHITE is (1) a basic bismuth nitrate or oxychloride (*v.* BISMUTH); (2) a preparation of mother-of-pearl.

PEARL-HARDENING (*Satin spar* or *Annaline*) is the trade name for artificial crystallised calcium sulphate. It may be prepared by treating calcium chloride solution with dilute sulphuric acid; by boiling waste gypsum with hydrochloric acid (Eng. Pat. 1577, 1897) or by the double decomposition of sodium or magnesium sulphate with calcium chloride (Eng. Pat. 7797, 1891). It is used in paper manufacture as a filling for writing paper (*v.* CALCIUM).

PEARLITE. The name given by Sorby (J. Iron and Steel Inst. 1886, 140; 1887, 255) to the eutectic mixture of ferrite and cementite present in steels. It may consist of alternate lamellæ of the constituents, which in oblique light show iridescent colours like mother-of-pearl, or it may exist in granular or 'beady' forms (Benedicks, Métallurgie, 1909, 6, 567). The two constituents are identical with 'free' ferrite and cementite (Ledebur, Stahl. u. Eisen, 1887, 8, 742; 1891, 11, 294).

It is the principal, sometimes the only constituent of intermediate steels and under the microscope is characterised by polishing in relief or etching, when the cementite stands out from the softer ferrite.

PEARLS. Calcareous concretions formed by various molluscs, those used in jewellery being mostly obtained from the large pearl-oyster, *Avicula* (*Meleagrina*) *margaritifera* (Lam.). The analysis of several fine white pearls by Harley gave calcium carbonate, 91·72; organic matter, 5·94; water, 2·23 (Proc. Roy. Soc. 1888, 43, 461). The calcium carbonate is of the orthorhombic modification identical with the mineral aragonite, and the organic matter is chiefly conchiolin. The sp.gr. of pearls varies between 2·650 and 2·686. Most pearls present a concentric structure, having been formed by successive deposits around a nucleus, which may be a grain of sand, a parasitic organism, a fragment of seaweed, or some other foreign body which by irritating the mollusc stimulates the secretion of nacre. The pearls are usually found in the mantle, but sometimes in the muscles of the mollusc; or, having escaped from the tissues, they may become adherent to the shell. To be valued by the jeweller, the pearl should be of spherical form, while its skin or outer coat should display the delicate iridescent sheen known as the 'orient.' Pearls of more or less hemispherical shape, cut from the shell, are termed *boutons*; while those which are warty or irregular in form pass under the name of *baroque.* Occasionally the pearl is found completely embedded in the mother-of-pearl. Some pearls, instead of showing a concentric structure, are crystalline, being composed of striated prisms radiating from the centre, and these may or may not possess a nucleus (Harley, Proc. Roy. Soc. 1889, xlv. 612).

The principal pearl fisheries are those of Torres Straits and the north-west coast of Western Australia, the Sulu Archipelago, Ceylon, and the coast of Madras, the Persian Gulf, and the Gambier and Pomotou Islands. The American fisheries are chiefly in the Caribbean Sea, off the coast of California, and near Panama. The pearls are mostly derived from *Meleagrina Californica* (W. H. Dall, Americ. Nat. 1883, 17, 579, 731; E. W. Streeter, Pearls and Pearling Life, London, 1886).

Coloured pearls are occasionally found, the tint in each case being dependent on that of the nacre lining the shell. The highly-prized black pearls are obtained chiefly from Mexico, and it has been suggested that the colour is due to the presence in the water of salts of silver, derived from neighbouring silver mines. Pearls have been artificially stained by means of silver salts. Pink pearls, sometimes finely water-lined, are mostly derived from the conch shell *Strombus gigas*; while large, coarse, yellowish pearls are obtained from the great clam, *Tridacna gigas.*

The principal source of fresh-water pearls is the pearl-mussel (*Unio margaritiferus*), a mollusc widely distributed in the rivers of northern temperate regions. It is found in the Tay, Forth, Earn, Doon, and many other mountain streams in Scotland. Scottish pearl-fishing was revived in 1860, and successfully carried on for some years by M. Unger. The pearl-mussel is also found in Cumberland; in Wales, especially in the Conway; and in Ireland. On the Continent pearl-fishing has been prosecuted in Saxony, Bohemia, and Bavaria; and in Norway, Sweden, and even Lapland. The American rivers also yield pearl-bearing molluscs, especially in New England, New Jersey, and Ohio; and in Canada (G. F. Kunz, Gems of N. America, New York, 1890). Fresh-water pearls are likewise obtained from China and Japan, and the Chinese exhibit much skill in inducing the formation of pearl by the artificial introduction of certain objects, upon which the mollusc deposits a nacreous layer. Chinese shells with images of Buddha formed of pearl adherent to the inner surface are well known to collectors (Macgowan, Journ. Soc. Arts, 1853, ii. 72).

The so-called cocoa-nut pearls, from the Malay Archipelago, are pearl-like bodies, resembling ivory, said to be found inside cocoanuts. Certain bodies which have been described as mammalian pearls are simply biliary concretions, formed mainly of cholesterol.

Artificial pearls are manufactured on the Continent in a variety of ways. Some are globes of thin opaline glass, filled with gum or wax, and deadened on the surface by means of hydrofluoric acid. The better kinds are glass globules lined with a nacreous composition, formed by digesting the silvery scales of the bleak in ammonia. Roman pearls are glass spheres, to which the nacreous material is applied externally. Celluloid, incorporated with fish scales, has become a favourite material for artificial pearls. Black pearls have been imitated by beads of a very compact hæmatite, which may be polished so as to present a kind of plumbago-lustre. Pink pearls are frequently confounded with beads of pale coral (*v.* MOTHER-OF-PEARL); Herdman and Hornell, Rep. Ceylon Pearl Fisheries (Roy. Soc. London, 1903); G. F. Kunz and C. H. Stevenson, The Book of the Pearl (New York, 1908).

F. W. R.

PEAT and TURF *v.* FUEL.

PEATWAX *v.* WAXES.

PELARGONIC ACID *v.* NONOIC ACIDS.

PELLETIERINE *v.* VEGETO-ALKALOIDS.

PELLITORY RESIN *v.* RESINS.

PENNETTIER'S GREEN. *Hydrated chromium sesquioxide v.* CHROMIUM.

PENNYROYAL, OIL OF, *v.* OILS, ESSENTIAL.

PENTADECATOIC ACID $C_{14}H_{29}COOH$, m.p. 51°, b.p. 257°.(100 m.m.), is obtained by the oxidation of methylpentadecylketone (Krafft, Ber. 1879, 1671) and by heating pentadecyl alcohol with potassium carbonate (Panics, Monatsh. 15, 14).

PENTAHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

PENTAL *v.* SYNTHETIC DRUGS.

Cyclo-**PENTANEDIONE** *v.* KETONES.

Cyclo-**PENTANONE** *v.* KETONES.

PENTLANDITE. A native sulphide of nickel (10–40 p.c.) and iron, (Fe,Ni)S, forming granular masses with a pale bronze-yellow colour. It is an important constituent of the extensively mined nickel ores of Sudbury in Ontario (*v.* PYRRHOTITE); and it has also been found in some quantity in the Essachossan mine near Inverary in Argyllshire, and at Lillehammer in Norway.

L. J. S.

PENTOSANS, PENTOSES *v.* CARBOHYDRATES.

PEPPER is the dried fruit of *Piper nigrum* (Linn.), a plant of the same family, *Piperaceæ*, as the Betel pepper and Long pepper.

It is a climbing plant, from 12 to 20 ft. high, growing in the East and West Indies and cultivated in many tropical countries. The fruit is borne on terminal flower stalks, 20 to 30 on each stem, the berries being about 5 mm. in diameter. It is gathered when it begins to turn red, dried in the sun or by artificial heat, after which it becomes black and shrivelled. Two crops are collected annually.

The chief varieties coming into the market at the present time are Mangalore (very little), Malabar, Ceylon, Java, and Tellicherry, Trang, Penang, and Singapore, the first mentioned being the most esteemed in the trade.

Preparation. Black pepper is the whole berry gathered in the green condition and dried in the sun or in the case of some varieties, as that of Singapore, over a fire.

White pepper is the same berry, gathered when more mature, but deprived of a portion of the pericarp or outer skin by macerating in water, drying, and then rubbing between the hands, from 6 to 12 p.c. of busks being thus obtained. The berries even after this are larger than those of Black pepper, but in no other respect does the greater degree of ripeness show itself.

Composition. The constituents to which the flavour and aroma of pepper are due are a resin, an alkaloid, *piperine*, and a volatile oil. According to W. Johnstone, *piperidine* is also present, but this has been contradicted (Zeitsch. öffentl. Chem. 1904, 10, 137). The usual plant constituents, including much starch, make up the bulk of the material.

The following table shows the comparative composition of the two varieties.

TABLE I.

COMPOSITION OF PEPPER.

(Richardson, U.S. Dept. of Agriculture, Bureau of Chem. Bul. 13, II., 206).

	Black pepper	White pepper
Water . . .	8·0 to 11·0	8·0 to 11·0
Ash	2·75 ,, 5·0	1·0 ,, 2·0
Volatile oil . .	0·50 ,, 1·75	0·5 ,, 1·75
Piperine and resin	7·0 ,, 8·0	7·0 ,, 8·0
Starch . . .	32·0 ,, 38·0	40·0 ,, 44·0
Crude fibre . .	8·0 ,, 11·0	4·11 ,, 8·0
Albuminoids .	7·0 ,, 12·0	8·0 ,, 10·0

Pepper itself is mainly employed as a condiment, the shells being used for tinned foods, sausages, etc. Black pepper is *official* in the British Pharmacopœia, and like the volatile oil acts as a carminative and stomachic.

Adulteration. The number of different substances which have been recorded from time to time as adulterants of pepper is very large, but in this country but little sophistication has been detected of recent years.

Excessive proportions of mineral matters may be present, owing to the whole berries having been insufficiently cleansed from adherent earth; or to their having been coated with kaolin, French chalk, or similar material, so as to enable black pepper to counterfeit the white variety; a high ash may also result from the deliberate addition of mineral substances to the ground pepper.

The commonest adulterant, however, is added starch, that of rice being most frequently employed. Some years back, ground olive stones ('poivrette' or 'pepperette') were frequently met with in samples examined under the Food and Drugs Acts, and many prosecutions resulted. The husk removed from white pepper in the course of manufacture is frequently added to both black and white peppers, being in the latter case bleached. In white pepper it must certainly be regarded as an adulterant if the proportion of added husk is at all substantial, and numerous successful prosecutions have been recorded. The addition of long pepper (*Piper longum*) was formerly fairly common.

A more objectionable offence arises from the craze for whiteness in pepper, and it is hardly too much to say that, but for this, adulteration would be much less frequent. White pepper is bleached to make it whiter still, and fetches a higher price in consequence although very deficient in aroma. The exact process is kept secret, though it is believed to involve the use of bleaching powder or sulphurous acid. The bleaching process naturally removes much of the aroma and the purchaser pays a higher price for an impoverished product, which is much more likely to become mouldy in consequence of the treatment it has undergone.

Of the rarer adulterants which, however, still appear to be met with in America and elsewhere, may be mentioned spent ginger, mustard hulls, linseed meal, ground almond shells, sawdust and barium sulphate.

Detection of adulteration. (1) Microscopical examination. For the detection of added starch the ground sample should be examined in water or dilute glycerol without attempting to reduce the material to a very fine powder. The masses of starch granules, cemented together with protein substances, will then retain the form of the cells in which they were enclosed.

Comparatively few isolated starch grains will be seen in this case if the sample consists of pepper only, but foreign starches will be easily visible. Rice starch alone presents any difficulty owing to its small size and general resemblance to pepper starch. The granules of the latter vary from 0·5 to 5μ in diameter, are polygonal or round and show a distinct hilum under a high power. Those of rice, of similar shape, vary from 2 to 10μ in diameter and are also collected in aggregates which are never entirely broken up, and when the sample is examined in polarised light are easily picked out in the dark field from amongst the pepper masses by their much more brilliant appearance.

In examining microscopically for olive stones and for excess of pepper husk it is of advantage to obtain the coarser and heavier particles and examine them separately. This may be done by sifting through a 40 or 60 mesh sieve, by sedimentation in chloroform, or by removal of the starch by boiling with dilute hydrochloric acid. The structure of the particles may be rendered more easily visible by digesting for 2 or 3 days in chloral hydrate or by treatment with dilute nitric acid and potassium chlorate.

The most conspicuous structural elements of the outer shell are the spiral vessels and the hypodermal stone cells of the pericarp, distinguished from the stone cells of the endocarp (beaker cells) by their larger and more variable size (15 to 20μ and sometimes 100μ long), less regular shape, thicker walls and yellow brown colour. The polygonal beaker cells have pitted walls and are colourless.

In examining white pepper for added shell, care must be taken to see that the above-mentioned structures of the outer layer are present in substantial proportion. The inner layer is a normal constituent of white pepper, and may be found in considerable quantities in the cheaper grades, where its presence is regarded by the trade as legitimate, although the addition of the dietetically much more valuable outer pericarp is looked upon as an adulteration.

With polarised light, ground-olive stones are easily recognised as they stand out brightly in the dark field, and exhibit a reddish tint. Most of the structural elements of pepper remain almost dark, but long pepper exhibits a bluish tinge under these conditions.

Various methods of staining have been suggested which will render the presence of 'poivrette' visible to the naked eye, but they are used to greater advantage in conjunction with the microscope. Dilute caustic soda colours olive stones, and also bleached pepper husks bright yellow while pepper remains unchanged. A solution of aniline in strong acetic acid leaves pepper unaltered, but turns ground olive stones or almond shells yellow brown.

Mixed with a few drops of freshly made 1 p.c. solution of phloroglucinol in alcohol and a drop of concentrated hydrochloric acid added olive stones, almond shells and substances containing much lignified tissue are stained pale to dark red, while pepper is only slightly altered to the naked eye. (For other reactions, *see* Analyst, xx. 1895, 181.)

Chemical analysis. For the routine chemical examination, the ash and the ash insoluble in HCl should be first estimated, the analyst being guided as to further determinations by the results of the microscopic examination.

If the total ash exceeds 5·5 in the case of black pepper or 3 in the case of white pepper, added mineral matter may be suspected, and a more detailed analysis is required. The composition of the ash of pepper is as follows:—

TABLE II.

ASH OF PEPPER.

(Rottger, Arch. f. Hygiene, 1886, Bd. IV. 183, and Blythe.)

No. of samples	Black pepper. 4. Per cent.	White pepper. 2. Average.
K_2O . . .	24·4 to 34·7	6·13
Na_2O . . .	1·5 ,, 5·5	0·79
CaO	11·6 ,, 16·1	33·09
MgO . . .	3·3 ,, 13·0	10·59
Fe_2O_3 . . .	0·3 ,, 2·2	2·04
MnO_2 . . .	0·19 ,, 0·8	0·55
P_2O_5 . . .	8·5 ,, 11·1	30·05
SO_3	4·0 ,, 9·6	3·50
Cl	5·4 ,, 8·5	0·72
Silica or sand .	1·5 ,, 6·5	2·05
CO_2	14·0 ,, 20·0	10·96

The amount of foreign starch can only be arrived at indirectly by calculation from the proportion of fibre, or pentosans, or fixed ether extract. On account of the somewhat wide variations in the composition of genuine pepper, no single determination affords trustworthy evidence.

If ground olive stones, almond shell, or similar substances have been detected, the most useful determinations are those of the fibre and starch. The starch should be determined by the diastase method after previous extraction with alcohol and ether, or by Ewer's method (J. Inst. Brewing, 1898, 552). The fibre by boiling 2 grms. of the sample under an inverted condenser with 200 c.c. of 1·25 p.c. sulphuric acid, and, after filtering and washing, extracting for a like period with the same volume of 1·25 p.c. soda, the fibre being finally filtered, dried, and weighed on a tared filter or Gooch crucible. The ash should be deducted. (For a quick method, which, however, gives different results from the above, *see* Stokes, Analyst, 12, 14.) If the fibre in a white pepper much exceeds 5 p.c. and microscopical examination shows the presence of the outer portions of the shell, the excess of husk may be taken as roughly equal to the percentage of fibre less 5 multiplied by 3.

For special purposes, the estimation of the piperine may be required and should be carried out as follows:—

The dried alcoholic extract from 50 grms. of the sample is treated with caustic alkali to dissolve resins, etc., well washed on a filter with the same solution, then with water; the precipitate is next dissolved in alcohol, the latter evaporated and the residue redissolved in a small volume of alcohol, the piperine precipitated by the addition of water and collected on a tared filter, washed, dried, and weighed.

In the case of non-nitrogenous adulterants, the proportion of nitrogen affords a useful basis for calculation, as the nitrogen, other than that present in the piperine, is fairly constant in amount in genuine peppers. It is best, therefore, to determine total nitrogen by the Arnold-Gunning method (*i.e.* mixing 1 grm. of the sample with about the same weight of copper sulphate and red oxide of mercury and digesting with sulphuric acid and potassium sulphate in the usual manner for the ordinary Kjeldahl process). The nitrogen in the ether extract should then be determined in the same manner and deducted from the total nitrogen. The nitrogen figure for the ether extract, multiplied by 20·36, gives a rough measure of the piperine.

The following tables show the results of the analysis of pepper and of some of the most likely organic adulterants.

TABLE III.

Results of analyses of various varieties of Black and White pepper and of pepper shells by Winton, Ogden, and Mitchell; Winton and Bailey (An. Rep. Connect. Exp. Station 1898, 198-199; 1903, 158–164); and by Doolittle, Mich. Dairy and Food Dept., Bull. 34.

No. of samples	Black pepper 65			White pepper 35			Pepper shells 7	
	Max.	Min.	Average	Max.	Min.	Average	Max.	Min.
Moisture	12·95	8·09	10·26	14·47	8·04	10·90	11·01	7·00
Ash, total	8·04[1]	3·09	5·02	4·28	0·86	1·71	28·81	7·82
Ash, insoluble in HCl . .	2·59[1]	0·0	0·61	0·86	0·0	0·17	22·90	0·79
Ash, soluble in water . .	3·32	1·65	2·52	1·16	0·12	0·38	4·66	1·53
Starch (Diastase method) .	41·75	22·05	35·64	63·60	48·88	54·97	15·30	2·30
Ether extract, volatile . .	2·20	0·65	1·29	0·95	0·49	1·04	1·11	0·68
,, ,, non-volatile .	10·44	6·60	7·90	7·94	5·65	6·58	4·97	1·51
Fibre	18·89	10·05	11·88	7·65	0·10	3·87	32·15	21·06
Nitrogen, total . . .	2·53	1·86	2·15	2·14	1·85	1·99	2·36	1·72
Nitrogen in fixed ether extract	0·45	0·25	0·32	0·34	0·24	0·30	0·15	0·20
	in 20 samples			in 10 samples			in 3 samples	
Alcohol extract . . .	11·86	8·31	9·44	8·55	7·19	7·66	6·30	4·00

TABLE IV.

Analysis of pepper adulterants. (Campbell Brown, Analyst, 1887, 12, 24.)

——	Ash	Starch	Fibre	Soluble in boiling dilute acid	Soluble in dilute alkali
White poivrette .	1·33	none	48·48	38·32	14·08
Black ,, .	2·47	none	47·69	34·55	17·36
Ground almond shells . .	2·05	none	51·68	23·53	24·79
Ground olive stones	1·61	none	45·38	39·08	15·04

Standards. The United States standards for pepper are as follows:—

	Black pepper.	White pepper.
	Not to exceed	
Ash	7·0 p.c.	4·0 p.c.
Ash insol. in hydrochloric acid . .	2·0 ,,	0·5 ,,
Fibre	15·0 ,,	5·0 ,,
	not less than	
Starch . . .	25·0 ,,	50·0 ,,
Fixed ether extract .	6·0 ,,	6·0 ,,
Percentage of N. in fixed ether extract . .	4·0 ,,	3·25 ,,

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[1] These figures, obtained from Achein pepper, which often contains hollow kernels and shell in excess, were only approached in one other sample of the same kind. Apart from these the maximum figures would be—Ash 7·00 p.c. and insoluble ash 1·80 p.c.

Black pepper should be free from added pepper shells, pepper dust, and other pepper by-products.

Long Pepper is the fruit of *Piper officinarum* [(Miq.) C.DC.] and *P. longum* (Linn.) (N. O. *Piperaceæ*) which grows in the islands of the Malay archipelago, Bengal, and the Philippine islands.

The fruit spike has the form of catkins from 2 to 6 cm. long and 4 to 7 mm. wide in the case of *P. officinarum*, that of *P. longum* being shorter and broader. It consists of numerous minute berries disposed along and partly embedded in an elongated axis. It has an odour and flavour somewhat resembling ordinary pepper but weaker and less agreeable, the smell becoming decidedly objectionable on warming.

It contains about the same amount of volatile oil and about half the amount of piperine present in ordinary pepper, and owing to the fact that the fruit often trails on the ground the ash is liable to be high, owing to the inclusion of clay and sand from the adherent soil, to remove which no special steps are taken. The figures obtained by the analyses of five samples by Campbell Brown and by Winton, Ogden, and Mitchell, are as follows :—

	Max.	Min.
Total ash . . .	9·61 p.c.	8·10 p.c.
Ash insol. HCl. . .	0·22 „	0·15 „
Ether extract . .	7·24 „	4·90 „
Starch and matters convertible into sugar .	49·34 „	42·88 „
Fibre	15·70 „	5·76 „
Nitrogen . . .	2·30 „	2·00 „
Alcohol extract . .	8·67	
Starch by diastase .	39·55	

It does not come into the retail market, and its chief use is in the pickling and canning trade, and, formerly, at all events, for the adulteration of black and white pepper (*q.v.*), for which purpose it may be bleached.

It has been used medicinally as a stimulant and carminative. C. H. C.

PEPPER, CAYENNE. Cayenne pepper is the dried and powdered fruit of various small fruited species of *Capsicum* of which *C. fastigiatum* (Blume) and *C. frutescens* (Linn.) are the most important. The plant is indigenous in tropical America and is cultivated in hot and temperate climates in many parts of the world.

The fruit is elongated, conical, and has a shiny, bright red surface becoming dull red and shrivelled when dry. The pods are from ½ to 2 cm. long and contain numerous yellowish, flattened kidney shaped seeds, 3 to 4 mm. in diameter.

Paprika, a large fruited variety of *Capsicum annuum*, is grown in Hungary, Spain, Italy, France, and Turkey. The fruit is from 2 to 5 cm. long and has a bright red or yellow shiny surface, but has not the intensely hot and pungent flavour of cayenne pepper. It is used chiefly on the Continent.

Other varieties of *C. annuum* are also widely employed on the Continent and in America for pickling.

Pimiento is a large fruited pepper of bright red colour and very mild flavour, used for stuffing olives and as colouring matter.

Composition. The characteristic constituents are a red colouring matter, present only in the pod, soluble in ether, light petroleum, carbon disulphide, or chloroform, and an active principle *capsaicine*, $C_{18}H_{28}NO_3$, to which the characteristic flavour is mainly due, and which, though it preponderates in the pod, is also found in the seed (Micko, Zeitsch. Nahr. genussm. 1, 818; 2, 411). There is also a tasteless and odourless fixed oil and an oleoresin (*syn. capsicin*), which, as used in medicine, is a mixture of fat, resin, and various other substances extracted by the solvent employed (Alcohol, B.P. Codex; Acetone, U.S. Pharmacopeia). Analyses by Richardson (U.S. Depart. of Agric., Div. of Chem. Bull. 13, 1887) of *Capsicum annuum* yielded the following results :

TABLE I.

	Seed	Pod	Fruit
Loss at 100° C. . .	8·12	14·75	11·94
Albuminoids ($N \times 6{\cdot}25$) .	18·31	10·69	13·88
Fat (ether extract) .	28·54	5·48	15·26
Fibre	17·50	23·73	21·09
Ash	3·2	6·62	5·20

Cayenne pepper is mainly used as a condiment and also in canary and chicken foods. The whole fruit, ripe or unripe, appears in the market as capsicums or chillies, low grade fruits of large size being usually employed under these names for pickling, etc. The dried fruit of *Capsicum minimum* is ‘ official ’ in the British Pharmacopœia. Taken internally, it acts as a stomachic and carminative to the alimentary canal, externally as an irritant and vesicant.

Adulteration. Although a long list of adulterants is given in most text-books, cayenne pepper is rarely sophisticated in this country at the present time. The addition of foreign starches, such as wheat and rice, of mineral substances, gypsum and red ochre and, to mask the presence of light-coloured adulterants like starch and gypsum, such diverse materials as turmeric, ground redwood, and aniline dyes should still be looked for. Ground nutshells and olive stones have also been found comparatively recently.

Detection of adulteration. Microscopical examination will suffice to detect the adulterants of vegetable origin. The presence of foreign starches will be at once apparent. The very minute starch grains of cayenne pepper are only present in very small numbers, the quantity being dependent on the ripeness of the fruit when gathered, and are usually embedded in cells.

The microscopical appearance of cayenne pepper is very characteristic and comparison with a standard sample will enable any of the above-mentioned vegetable adulterants to be detected with comparative ease (*v.* PEPPER).

Preparations of the sample, both before and after removal of the fat, should be mounted in water or dilute glycerol. Fragments of the epicarp showing quadrilateral cells of which the walls have a slightly wavy outline, but are not beaded, and which are arranged in rows, serve to distinguish cayenne pepper from paprika. (For further details as to the structural differences between different species of capsicums, *see* Pharm. J. 1901, 13, 552 ; 1902, 69, 3 ; or Winton, Microscopy of Vegetable Foods.)

The presence of mineral adulterants will be indicated by a high ash; nutshells or olive stones will raise the proportion of fibre (estimated as in Pepper, *q.v.*). For the detection of oil, soluble vegetable or coal tar colours, the ether extract of the sample may be shaken with a mixture of 2 parts of carbon disulphide and 15 parts of ethyl alcohol. The carbon disulphide will dissolve the oil and the natural colouring matter of the capsicum, while most aniline colours will pass into the supernatant alcohol layer.

Table II. (Parry, "Food and Drugs") shows the limits within which the figures obtained by the analyses of cayenne pepper are found to vary, and Table III. gives figures for chillies and Table IV. for paprika.

TABLE II.

	Maximum	Minimum
Moisture	7·5	3·5
Ether extract, volatile .	2·8	0·7
,, ,, non-volatile	15·5	19·0
Alcohol extract . .	30·0	25·0
Starch by diastase method	1·5	0·8
Fibre	25·0	20·0
Nitrogen . . .	2·40	2·08
Ash, total . . .	7·2	5·0
,, soluble in water .	3·3	0·30
,, insoluble in HCl	0·3	0·05

TABLE III.

Analayses of whole chillies. (Zanzibar, Japan and Bombay. 8 samples in all.) (Winton, Ogden and Mitchell, Ann. Report, Connecticut Exper. Station, 1898, 200.)

—	Maximum	Minimum	Average
Moisture	7·08	3·67	5·73
Ether extract, volatile .	2·57	0·73	1·35
,, ,, non-volatile	21·81	17·17	20·15
Alcohol extract . .	27·61	21·52	24·35
Starch (diastase method)	1·46	0·80	1·01
Fibre	24·91	20·35	22·35
Nitrogen, total . .	2·34	2·13	2·18
Ash, total	5·96	5·08	5·45
,, soluble in water .	4·93	3·30	3·98
,, insol. in HCl . .	0·23	0·05	0·15

TABLE IV.

Analysis of paprika (whole pods). (Doolittle and Ogden, J. Amer. Chem. Soc. 30, 1908, 1481.)

—	Maximum	Minimum	Average
Loss at 100°C. . . .	9·39	7·26	8·52
Ether extract, volatile . .	1·25	0·17	0·93
,, ,, non-volatile .	11·99	7·42	9·57
,, ,, ,,			
Iodine number . . .	136·8	130·3	133·5
Reducing matters (acid conversion) as starch . .	21·4	16·52	19·46
Fibre	19·83	15·1	15·33
N×6·25	17·44	14·06	15·51
Ash total	7·06	5·24	6·22
,, soluble in water . .	5·79	4·59	5·14
,, insol. HCl . . .	0·22	0·05	0·08
Alkalinity of ash, total . .	8·00	6·10	7·04
,, ,, sol. in water	5·70	4·07	4·93

Standards. The official standard of the U.S. Department of Agriculture for cayenne pepper provides that it shall be the dried ripe fruit of *C. frutescens*, *C. baccatum*, or any small fruited species of capsicum, and that the fixed ether extract should not be below 15 p.c., the total ash not more than 6·5 p.c., the ash insoluble in HCl not more than 0·5 p.c., starch (diastase method) not more than 1·5 p.c., and fibre not more than 28 p.c. C. H. C.

PEPPERMINT. The *Mentha piperita* (Linn.) of Europe and America; *M. arvensis* (Linn.) of Japan. Extensively grown for the sake of its volatile oil, which is procured by distilling its leaves. The oil and the preparations made from it are used as aromatics, carminatives, and stimulants, and are useful in medicine for griping pains. It is also employed in the form of mint-camphor, or menthol, for outward application in affections of the nerves (*v.* OILS, ESSENTIAL).

Oil of peppermint amounts on the average to 0·8 of the total plant used. The crystals of peppermint camphor are obtained from the distillate by cooling; the oil having been drained off, the process is repeated, when a tolerably pure oil is secured. After a third repetition no crystallisation takes place.

Menthol, or peppermint-camphor, in its commercial state is a white crystallised mass, melting at about 35° and boiling at 210°. When purified by distillation the melting-point is raised to 42° and the boiling-point to 212°.

Menthone $C_{13}H_{10}O$ is a colourless mobile liquid, neutral to test papers, soluble in almost all proportions in alcohol, chloroform, benzene, and carbon disulphide, but insoluble in water. It stands to menthol in a similar relation to that in which camphor stands to borneol, as is shown by the fact that menthol can be reproduced from its ketone $C_{13}H_{10}O$ by a reaction similar to that by which borneol is produced from camphor.

Menthene $C_{10}H_{10}$ is a colourless liquid of an agreeable odour, moderately soluble in ether or alcohol, more so in benzene, turpentine, and petroleum. It may be prepared by heating menthol with zinc chloride. See J. Moss (Pharm. J. [iii.] 5, 566); J. Mackay (*ibid.* [iii.] 5, 825); Beckett and Wright (Chem. Soc. Trans. 1876, 1, 1); M. Moriya (*ibid.* 1881, 39, 79); Atkinson and Yoshida (*ibid.* 1882, 41, 49) (*v. Peppermint camphor*, art. CAMPHORS *v.* TERPENES).

PEPPERMINT CAMPHOR *v.* CAMPHORS.

PEPPERMINT OIL *v.* OILS, ESSENTIAL.

PEPSIN. *Pepsinum* (*Pepsine*, Fr.; *Pepsin*, Ger.). Pepsin is a ferment or enzyme, existing in the acid secretion of the mucous membrane of the stomach or gastric juice. It possesses the property, in presence of dilute acid, and, within certain limits of temperature, of converting albuminous food into soluble assimilable peptone. Schwann (Müller's Arch. 1836) made the first attempt to prepare the ferment in a form available for supplying artificial digestion in cases where the natural function was imperfectly performed. To obtain a good product and to preserve it requires great care and skill. The animals generally selected are the hog, sheep, and calf, and the preparation usually employed is simply the dried mucous membrane of the stomach. Details of preparation are given by Beale (Med. T. Gaz. 1872, 1, 152), Wasmann (Lehm. Phys. Chem. 2, 40), Brücke (Sitz. Ber. 43, 601), Schmidt (Annalen, 61, 22), Liebreich (Practitioner, March 1877), Petit (J. Pharm. Chim. [v.] 2, 85),

Chapoteaut (Compt. rend. 95, 140), Maly (J. pr. Chem. [ii.] 11, 104), Wittick (J. 1870, 894), Meissner (Z. Rat. Med. 7, 1; 8, 280; 10, 1; 12, 46; 14, 78 and 303); also Scheffer (Amer. J. Pharm. 42, 98; 43, 3; Pharm. J. [iii.] 1, 666; 2, 761, 783), Selldon (*ibid.* [iii.] 4, 89), Long (Med. Press. Cir. 8, 300), Kinkead (Lancet, 1870, 2, 667), Farr (Med. T. Gaz. 1871, 1, 302), Rennard (J. 1874, 944), Zwick (Amer. J. Pharm. 43, 261), Audouard (Year-Book Pharm. 1878, 343), Pekelharing (Zeitsch. physiol. Chem. 22, 233), Nencki and Sieber (*ibid.* 32, 291), Schrumpf (Beit. chem. Physiol. Path. 6, 396).

Pepsin of commerce varies much in activity (Tuson, Lancet, 1870, 2, 212; Grierson, Year-Book Pharm. 1887, 263). 5 milligrams digested with 12·5 grams of coagulated and firm white of fresh eggs and 125 c.c. of acidified water containing about 0·2 p.c. of hydrogen chloride at 40·5° for 6 hours with frequent shaking should give an almost clear solution, containing only a few small flakes. This method of testing, which is adopted by the Pharmacopœia, is the outcome of numerous investigations as to the effect of different temperatures and different forms of albumen, together with the selection of an acid and determination of its appropriate strength. Compare Petit (J. Pharm. Chim. [v.] 1, 82; 2, 85), Benger (Pharm. J. [iii.] 12, 270, 415), Grützner (Zeitsch. anal. Chem. 1874, 106), Vigier (J. Pharm. Chim. [v.] 9, 398; 9, 461; 10, 17), Schlickum (Year-Book Pharm. 1886, 96), Dastre (Compt. rend. Soc. Biol. 1894, 778), Croner (Virchow's Archiv. 150, 230), Harlay (J. Pharm. Chim. [vi.] 10, 105).

Peptic activity is inhibited or destroyed by antiseptics (Grober, Pflüger's Archiv. 104, 109), certain bacteria (Papasotiriou, Arch. Hygiene, 57, 269), or by shaking (Shaklee and Meltzer, Proc. Amer. Physiol. Soc. 1908, 29).

In addition to the method given above, various other methods have been devised for the determination of peptic activity (Samojloff, Pflüger's Archiv. 85, 86; Meunier, J. Pharm. Chim. [vi.] 14, 555; Kuttner, Zeitsch. physiol. Chem. 52, 63; Fuld and Levison, Biochem. Zeitsch. 6, 473; Einhorn, Chem. Zentr. 1908, ii. 1295).

On the question of the identity of pepsin and rennin, *see* Schmidt-Nielsen (Zeitsch. physiol. Chem. 48, 92), Gewin (*ibid.* 54, 32), Bang (*ibid.* 54, 359), Hammarsten (*ibid.* 56, 18), Herzog (*ibid.* 60, 298), Taylor (J. Biol. Chem. 5, 399).

A. S.

PERCARBONATES $M_2C_2O_6$, may be prepared by electrolysing a strong solution of the normal carbonates at −30° to −40° (Riesenfeld and Reinhold, Ber. 1909, 42, 4377). The potassium salt is a bluish-white, amorphous deliquescent powder which decomposes on heating into potassium carbonate, carbon dioxide and oxygen, and is a strong oxidising and bleaching agent. When added to a neutral solution of potassium iodide, it immediately liberates iodine thus: $K_2C_2O_6+2KI=2K_2CO_3+I_2$; no oxygen being evolved. The above authors regard this action as characteristic for the percarbonates, and therefore maintain that the 'percarbonates,' such as Na_2CO_4, obtained by the action of hydrogen peroxide on sodium carbonate (Tanatar, Ber. 1899, 32, 1544; J. Russ. Phys. Chem. Soc. 1902, 34, 952), are additive compounds of carbonates and hydrogen peroxide. This contention is, however, denied by Tanatar (Ber. 1910, 43, 127, 2149; *see* also Wolffenstein, *ibid.* 639; Riesenfeld, *ibid.* 566, 2594).

The only percarbonates which have been prepared are those of the alkali metals, and of barium (Wolffenstein and Peltner, Ber. 1908, 41, 271). Sodium hydrogen percarbonate

$$4Na_2CO_4,H_2CO_4$$

has been used as a disinfectant and in the preparation of hydrogen peroxide (D. R. P. 188569).

PEREZONE. An alcoholic solution of pipitzahoic acid obtained from the rhizomes of *Perezia adnata* (A. Gray), found in Mexico. It is extremely sensitive to alkalis, which colour it rose-mauve, and may be used as an indicator.

PERFUMES (SYNTHETIC). Prior to 1875 perfumes were prepared almost entirely from plants by various processes of distillation and extraction (*v.* Oils, Essential); musk and civet, used from the very earliest times, were of animal origin; synthetic perfumes were unknown. To-day, almost every flower-perfume may be imitated by a so-called 'synthetic oil,' the odour of which closely resembles that of the natural product. The faithfulness of the imitation varies very much with the different scents; it is doubtful, for instance, whether any purely synthetic violet or rose oil at present in existence can vie with the natural fragrance. The term 'synthetic' thus applied is misleading: the 'synthetic oils' are in fact mixtures of a number of chemical compounds, some of which have been obtained by synthetic processes, others merely isolated from the essential oils in which they occur. In many cases, the most satisfactory results are only obtained by blending the 'synthetic' with a natural oil. Thus, jasmine oil is added with good effect to the 'synthetic' oils of rose, lilac, muguet, &c.; the ketone (jasmone) characteristic of jasmine oil has been isolated, but its composition has not as yet been determined, and no synthetic substance hitherto obtained is entirely satisfactory in replacing it. In certain cases where the constitution of the characteristic constituent of a particular perfume has not been elucidated, the substitute may consist of a substance possessing an entirely different structure from that of the natural product yet closely resembling it in smell. Thus the characteristic principle of musk is a non-nitrogenous ketone of unknown constitution: synthetic musk consists, however, of various di- or trinitro-derivatives of tertiary butyl toluene.

The synthetic perfume industry may be said to have originated with the manufacture of vanillin from eugenol, described in a patent taken out by Tiemann in 1876 (Eng. Pat. 1161); shortly afterwards in 1879, coumarin and heliotropin were prepared, and since that time the production of synthetic substances for use in the blending of perfumes has steadily continued.

Not only is the scent of an oil modified by the presence of minute traces of odoriferous substances, but the degree of dilution is an important factor in producing the requisite odour. The solvent most commonly used is a 95-96 p.c. ethyl alcohol. The condition of the alcohol is of great importance; it must be free from fusel oil; and taste, smell, and colour must give no indication of impurities. Methyl alcohol finds little application, largely owing to the fact that the commercial alcohol contains more or less acetone, which has an injurious effect. 95 p.c. alcohol is also used for preparing the infusions of the flower pomades, 1250 kilos. of solvent being used to extract 1000 kilos. of pomade. The extraction is twice repeated so that three infusions are obtained, diminishing in strength. For the cheaper sorts of extracts and toilet-waters, the rectified spirits of wine is replaced by potato spirit.

The least soluble of the synthetic perfumes are the artificial musks, of which less than 1 p.c. dissolves in alcohol. Benzyl benzoate and benzyl cinnamate are used as solvents for these, 1 kg. of the former dissolving 500 grams ketone moschus or 250 grams Musc Baur.

The extracts which are sold as handkerchief perfumes are known as quadruple, triple, double, and simple, according to their strength; 12 parts of a triple extract will furnish 20 parts of double or 30 parts of simple extract by dilution with alcohol and water; in the preparation of the double and simple extracts, the second infusions of the flower pomades are also utilised.

For the preparation of aqueous and dilute alcoholic toilet waters, only a limited number of substances are available, owing to the sparing solubility of the majority of perfumes in water. The most soluble are phenyl ethyl alcohol (2 p.c.), benzyl alcohol (1 p.c.) and vanillin (0·8 p.c.).

Relation between constitution and smell.—Our knowledge of the relations between the chemical constitution of a compound and its odour is very scanty. Within the same class of compounds, there is a general resemblance, and there is a gradual change of odour in passing from one member of a homologous series to the next, well-marked, for instance, in such a series as that of the fatty esters. Austerweit and Cochin (Compt. rend. 1910, 150, 693) have studied the effect of the alkyl substituents on the geraniol and citronellol molecules. In citronellol, the introduction of one methyl or ethyl group is accompanied by a marked odour of tea roses: a second methyl or ethyl group is described as producing an odour of roses with a faint odour of camphor. But if the substituent be a propyl or butyl radicle, the rose odour almost vanishes: if phenyl be the entering radicle, the rose odour is much augmented. In geraniol, the introduction of one or two methyl groups produces a smell of pelargonium leaves; the ethyl group appears to leave unaltered the odour of the original geraniol. The effect of the position of the aldehyde group in the *cyclo*geraniolene ring was studied by Merling and Welde in their work on ionone (Annalen, 1909, 366, 119). Their conclusion is that aldehydes which are derived from *cyclo*geraniolene form with acetone products possessing the odour of violets if the aldehyde group is adjacent to the methyl groups. The intensity of the odour increases with the number of methyl groups which are adjacent to the aldehyde group; if, however, the latter be removed from the proximity of the methyl groups, the odour vanishes. In his work on the nitrobutylxylenes (Artificial Musks), Baur has also studied the effect of the position of the substituents in the benzene nucleus on the smell (Ber. 24, 2832). It is, however, difficult to draw any general conclusions: we are met with startling anomalies, such as the well-known resemblance between the odours of benzaldehyde and nitro-benzene, and little can be said save that the part played by unsaturated groupings is important. The subject is particularly difficult to investigate, since our sensation offers only a vague means of classifying and measuring smell.

The list of substances, used in the compounding of perfumes is a long one. The most important of these are as follows:

Hydrocarbons. With the exception of styrene and *p*-cymene, the hydrocarbons which occur in the natural perfumes and contribute to their odour belong to the terpene group. Pinene, with its characteristic odour of pine-needles, is the chief constituent of pine-needle oil; *d*-limonene occurs in the oils of lemon, orange, orange-flower, bergamot, &c.: menthene is found in oil of peppermint and carvene in caraway oil (*v.* TERPENES). The halogen derivatives and α-chloro- and α-bromo-styrolene are used in the preparation of oil of hyacinth.

Alcohols. The saturated fatty alcohols occur commonly as esters; the alcohols of the terpene and of the aromatic series are either free or in combination with fatty acids. The latter are used in preparing, amongst others, the oils of rose, jasmine, hyacinth and lilac.

OLEFINIC TERPENE ALCOHOLS.

Citronellol $C_{10}H_{20}O$

$CH_2:C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2OH$

$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CH_2OH$

b.p. [*d* -citronellol] (17 mm.) 117°–118°; sp.gr. 0·8565 at 17·5°; $[\alpha]_D + 4°$ at 17·5°; n_D 1·45679; b.p. [*l* -citronellol] (15 mm.) 113°-114°; sp.gr. 0·8612 at 20°; $[\alpha]_D -4° \ 20'$; n_D 1·45789 (Tiemann and Schmidt, Ber. 1896, 29, 906).

d-Citronellol occurs in geranium and in Java citronella oils; *l*-citronellol has been isolated from geranium and from rose-oils. Prolonged discussion has taken place as to the identity of citronellol with the alcohols, 'rhodinol,' 'reuniol,' and 'roseol' isolated from geranium or rose-oil. It is now accepted that the last two are mixtures of citronellol with geraniol. The evidence as to the chemical identity of the *l*-rhodinol, described by Barbier and Bouveault (Compt. rend. 1897, 124, 1308), is somewhat conflicting, for Schimmel & Co. (Report, Oct. 1904, 123) showed that citronellol obtained by the reduction of citronellal gave a pyroracemic ester, the semi-carbazone of which was identical with that similarly obtained from rhodinol, each melting at 110°-111°. The most satisfactory explanation of the discrepant results obtained by different observers appears to be that recently offered by Harries and Himmelmann (Ber. 1908, 41, 2187), who, from studying the action of ozone on the citronella compounds, arrived at the conclusion that citronellol consists of a mixture of two isomerides, differing in the position of the double bond as represented above. By the action of ozone on citronellol, 20 p.c. of acetone is produced corresponding to 20 p.c. of the rhodinol structure $(CH_3)_2C{=}C{<}$. The evidence for the formula of citronellol is based chiefly upon the behaviour of the corresponding aldehyde, citronellal (*v. infra*).

Citronellol occurs in company with geraniol: the boiling-points of both alcohols lie very close to each other, but geraniol is the less stable and may be destroyed by heating with phthalic anhydride at 200° or with benzoyl chloride at 140°–160° (Barbier and Bouveault, Compt. rend. 1896, 121, 530). Citronellol may be obtained from citronella oil by reducing with sodium amalgam and acetic acid when the aldehydes citral and citronellal are reduced to citronellol. The mixture of geraniol and citronellol is then treated with phosphorus trichloride in ethereal solution at a low temperature: a phosphite of citronellol is formed which is extracted by water, geranyl chloride remaining in the ethereal layer (Tiemann, Ber. 1896, 29, 921).

Cold dilute $KMnO_4$ oxidises citronellol to a polyhydric alcohol, converted by chromic acid mixture to acetone and β-methyl adipic acid. It is characterised by a liquid phthalic acid ester giving a crystalline silver salt, and by its oxidation to citronellal, the latter being identified by its semi-carbazone (m.p. 84°) or its compound with β-naphthocinchoninic acid.

The isomeric alcohols of the formula $C_{10}H_{18}O$, *linalool*, *geraniol*, and *nerol*, readily undergo mutual transformation. Thus if geraniol be heated at 200° with water in an autoclave, linalool is formed (Schimmel Report, April, 1898, 25). When treated with hydrochloric acid, geraniol is converted into linalyl chloride, from which linalool may be obtained by the action of alcoholic potash or of a solution of silver nitrate (Tiemann, Ber. 1898, 31, 832; 1895, 28, 2138). On the other hand, by the action of acetic anhydride on linalool, a mixture of the acetates of geraniol, nerol, and terpineol is formed (Tiemann and Schmidt, Ber. 1895, 28, 2137; Tiemann and Semmler, *ibid.* 1893, 26, 2714; Stephan, J. pr. Chem. 1898, [ii.], 58, 109; Zeitschel, Ber. 1906, 39, 1780). They frequently occur together and have all three been detected in the oils of rose, neroli, petit grain and linaloe.

Linalool $C_{10}H_{18}O$

$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3)(OH)CH:CH_2$ or

$CH_2:C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3)(OH)CH:CH_2$

b.p. 198°–199° (13 mm.) 88·3°–89·5°: sp.gr. 0·870 at 15°, $n_D^{20°}$ 1·4668 (Gildmeister, Arch. Pharm. 1895, 233, 179); *l*-linalool $[\alpha]_D$ −20° 7′: *d*-linalool $[\alpha]_D$ + 19° 8′ (Stephan).

Linalool is the chief constituent of linaloe oil; it occurs as the *l* form in the oil from Cayenne, and both as *d* and *l* forms in that from Mexico. Amongst other oils in which it has been detected are coriander (*d*), sweet orange (*d*), nutmeg (*d*), ylang-ylang (*l*), rose (*l*), reunion geranium (*l*), petit-grain (*l*), bergamot (*l*), neroli (*l*), lemon (*l*); in the four last of these and in lavender and jasmine-flower oils, it is also present as the acetate; the butyrate occurs in lavender oil and the *iso*butyrate in Ceylon cinnamon oil and the *iso*valerate in the oil of sassafras leaves. It is isolated by fractional distillation and purified by the action of phthalic anhydride on its sodium compound; sodium linalyl phthalate is soluble in water and after saponifying with alcoholic potash, the linalool may be extracted with ether. Citral is obtained by oxidation with chromic acid mixture (Bertram and Waldbaum, J. pr. Chem. 1892, [ii.] 45, 599).

Dilute $KMnO_4$ in the cold oxidises it to polyhydric alcohols, which are converted by chromic acid mixture into acetone and laevulic acid (Tiemann and Semmler, Ber. 1895, 28, 2130); by reduction with nickel and hydrogen, 2:6-dimethyl octane has been obtained (Ber. 1908, 41, 2083).

It may be identified by its phenyl urethane (m.p. 65°–66°) or its α-naphthyl urethane (m.p. 53°) or it may be oxidised to citral.

Geraniol $C_{10}H_{18}O$

$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3):CH{\cdot}CH_2OH$

b.p. (17 mm.) 120·5°–122·5°; sp.gr. 0·8894 at 20°; n_D^{20} 1·4766 (Tiemann and Semmler, Ber. 1893, 26, 2711).

Geraniol forms the chief constituent of Palmarosa and of German and Turkish rose oils and occurs in geranium, citronella, lemongrass, and many other oils. It is also found as acetate, *iso*valerate, *n*-caproate, and tiglate. It is isolated by fractional distillation and purified either by means of its crystalline compound with calcium chloride (Bertram and Gildmeister, J. pr. Chem. 1896, [ii.] 53, 233; 1897, 56, 507), or by treating its sodium compound with phthalic anhydride in benzene solution (Tiemann and Krüger, Ber. 1896, 29, 1901). By oxidation with chromic acid mixture, citral is obtained (Tiemann, Ber. 1898, 31, 828), from which geraniol may again be obtained by reduction. The catalytic action of copper at a high temperature has also been utilised for the oxidation of geraniol to citral (Bouveault, Bull. Soc. chim. 1908, [iv.] 3, 119). The action of chromic acid mixture after treating with $KMnO_4$, produces acetone, laevulic, and oxalic acids (Semmler, Ber. 1893, 26, 2720). Geraniol is more stable than linalool to the action of acids and is quantitatively converted by acetic anhydride into geranyl acetate. By the action of dilute H_2SO_4, terpin hydrate is obtained (Tiemann and Schmidt, *ibid.* 1895, 28, 2138): concentrated formic acid reacts forming α-terpineol, terpinene and dipentene (Bertram and Gildmeister, J. pr. Chem. 1894, [ii.] 49, 195; Stephan, *ibid.* 1899, [ii.] 60, 244). The phthalic acid ester (m.p. 47°), the α-naphthyl urethane (m.p. 47°–48°), and the di-phenyl urethane (m.p. 124°) are characteristic.

Nerol $C_{10}H_{18}O$, stereoisomeric with geraniol; b.p. 226°–227°: 125° (25 mm.); sp.gr. 0·8813 at 15°; occurs in neroli-oil, chiefly as acetate (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 502), in rose, linaloe, and petit grain oils, and in the oil of *Helichrysum angustifolium* (Heine & Co., D. R. P. 209382). It may be obtained by the action of acetic anhydride on linalool (Zeitschel, Ber. 1906, 39, 1780): about 5 p.c. is formed on reducing citral. It has a rose-like smell and in chemical behaviour resembles geraniol. Nerol does not, however, give a crystalline compound with $CaCl_2$ and reacts with dilute H_2SO_4, forming terpin hydrate more readily than does geraniol. Its di-phenyl urethane melts at 52°–53°.

CYCLIC TERPENE ALCOHOLS.

Terpineol *v.* Terpenes.
Borneol *v.* Camphors.
*iso***Borneol** *v.* Camphors.

AROMATIC ALCOHOLS.

Benzyl alcohol $C_6H_5{\cdot}CH_2OH$; b.p. 205°, sp.gr. 1·05 at 15°, $n_{\rm D}^{20^\circ}$ 1·540; occurs free in tuberose, ylang ylang, carnation, jasmine oils, &c., as acetate in ylang ylang, hyacinth, and jasmine oils, as benzoate (ylang ylang), cinnamate, salicylate (ylang ylang), and phenyl acetate (neroli). It is manufactured by the action of lead oxide at 100° or of potassium carbonate on benzyl chloride, or by the action of potassium acetate and saponification of the acetate formed. It is characterised by a phenyl urethane (m.p. 78°), a phthalic acid ester (m.p. 106°–107°), and a semi-carbazone of its pyroracemic ester (m.p. 176°).

Phenyl ethyl alcohol $C_6H_5{\cdot}CH_2{\cdot}CH_2OH$; b.p. 220°–222° (740 mm.), sp.gr. 1·2042 at 15°, $n_{\rm D}^{20^\circ}$ 1·53212; occurs in rose and neroli oils as benzoate and phenyl acetate. In preparing rose-oil by steam distillation, much of the phenyl ethyl alcohol is lost. It is obtained by reducing (1) phenyl acetaldehyde with sodium amalgam, and (2) phenyl acetic ester with sodium and alcohol; in its manufacture other methods are probably used. It is purified by means of its compound with calcium chloride (Bouveault and Blanc, D. R. P. 164294; Compt. rend. 1903, 136, 1676; 1903, 137, 60). It may be separated from citronellol and geraniol by its greater solubility in dilute alcohol. The phenyl urethane melts at 80°, the phthalic acid ester at 188°–189°.

Phenyl propyl alcohol $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$; b.p. 235°, sp.gr. 1·007 at 15°. This alcohol, hyacinth-like in odour, is obtained by reducing cinnamic ester with sodium and alcohol (Schimmel, D. R. P. 116091) or by reducing benzyl aceto-acetic ester (Bouveault and Blanc, D. R. P. 164294). The phenyl urethane melts at 47°–48°.

Cinnamic alcohol (*v.* Cinnamic Alcohol).

ESTERS.

The methods used in the preparation of the esters are (1) the action of hydrochloric acid on a mixture of alcohol and acid; (2) the action of the alcohol or its sodium compound on the fatty acid anhydride or chloride, the reaction on the large scale being carried out in pyridine solution.

In preparing the esters of those olefinic terpene alcohols which themselves undergo change on heating with acid reagents, a mixture of the alcohol and acid may be treated with small quantities of a mineral acid below 30° (Bertram, D. R. P. 80711).

The fatty acid esters find wide application as fruit essences. A list of those more especially used in perfumery is appended.

Ester	Boiling-point	Synthetic oil in which used
Bornyl formate	90° (10 mm.)	Lime blossom
Citronellyl ,, .	97°–100° (10 mm.)	Geranium
Geranyl ,, .	119°–121° (15 mm.)	,,
Amyl acetate	112° (760) 38° (12 mm.)	
Benzyl ,,	262° (760)	Jasmine
Bornyl ,,	98° (10 mm.)	
Geranyl ,,	128°–129° (16 mm.)	Rose
Linalyl ,,	97° (10 mm.)	Bergamot
Phenyl ethyl ,,		Orange flower
Terpineol ,,	110°–115° (10 mm.)	Bergamot, Lilac
Geranyl propionate . . .		Bergamot
Geranyl butyrate		Geranium
Geranyl caproate		,,
Ethyl œnanthylate		
Ethyl pelargonate		

A large number of patents deal with the preparation of the esters of the cyclic terpene alcohols: thus in preparing *iso*borneol esters, camphene and the fatty acid may be heated with P_2O_5 (Schindelmeiser, D. R. P. 229190), pinene hydrochloride warmed with the fatty acid, and anhydrous zinc sulphate (D. R. P. 196017), &c.

Amongst the aromatic acid esters used are:

Ester	Boiling-point	Synthetic oil in which used
Methyl benzoate	199·2° (746 mm.)	Ylang-ylang, hyacinth
Ethyl ,,	211°–212° (729 mm.)	Ylang-ylang
Benzyl ,,	323°–324°	Largely used as a solvent for non-alcoholic perfumes, *e.g.* artificial musks
Phenyl ethyl ,,		Hyacinth
Linalyl ,,		Ylang-ylang
Methyl salicylate	217° (730 mm.)	Oil of winter-green
Ethyl ,,	234° (743 mm.)	
Amyl ,,	276°–277° (743 mm.)	Clover

The esters of the unsaturated and ketonic fatty acids also find considerable application. The *αβ*-unsaturated acids, *e.g.* nonylenic acid, may be prepared by condensing aldehydes with malonic acid in pyridine solution (Weizmann and Harding, Chem. Soc. Trans. 1910, 97, 299).

The acetylene carboxylic acids are prepared by acting on the sodium compounds of the acetylene hydrocarbons with CO_2 in ethereal solution. Heptine (C_7H_{12}) and octine (C_8H_{14}) are thus converted to *octinic* and *noninic* acids; on boiling these with alcoholic caustic potash, esters of *β*-ketonic acids are obtained (Moureu, D. R. PP. 132802, 1902; 133631; 158252, 1905).

These esters are also directly prepared by treating the sodium compounds of the hydrocarbons with chloroformic ester in ethereal solution.

PHENOLS AND THEIR ETHERS.

*iso***Eugenol** (*v.* Eugenol).
Anethole (*v.* Anethole).
Thymol (*v.* Phenol and its Homologues).
Naphthol (*v.* Naphthalene).

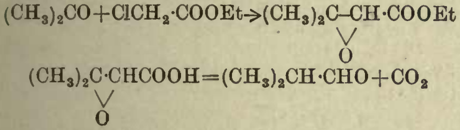
The methyl and ethyl *β*-naphthyl ethers are both known as nerolin, the former as yara-yara, the latter as bromelia. In very dilute solution, the odour resembles that of orange-flower.

ALDEHYDES.

General methods used for the production of higher fatty aldehydes are—

(1) The reduction of the ester of the corresponding acid to the alcohol and subsequent oxidation of the alcohol, heated copper being used as the catalytic agent.

(2) The method of Darzens (D. R. P. 174239, 174279), by which a ketone is condensed with chloracetic ester in the presence of an alkaline condensing agent; on heating the glycidic acid thus obtained, CO_2 is evolved and the aldehyde formed. A large number of aldehydes have been produced by this method.



$$(CH_3)_2CO + ClCH_2{\cdot}COOEt \rightarrow (CH_3)_2\underset{\diagdown\, O\, \diagup}{C{-}CH}{\cdot}COOEt$$

$$(CH_3)_2\underset{\diagdown\, O\, \diagup}{C{\cdot}CH}COOH = (CH_3)_2CH{\cdot}CHO + CO_2$$

Higher fatty aldehydes have been detected in oils of rose, lemon, &c.

n-**Octaldehyde** $C_8H_{16}O$; b.p. 60°–63° (10 mm.), sp.gr. 0·827 at 15°, n_D 1·41955. Prepared from octyl alcohol (Schimmel, Rep. 1899, 25). The β-naphthyl cinchoninic acid derivative melts at 234°.

n-**Nonaldehyde** $C_9H_{18}O$; b.p. 80°–82° (13 mm.), sp.gr. 0·8277 at 15°, $n_D^{16°}$ 1·42452. First detected in rose-oil (Schimmel, Rep. 1900, 53) and subsequently in orris, cinnamon, mandarin and lemon oils.

A yield of 71 p.c. is obtained by distilling α-hydroxydecoic acid (Bagard, Bull. Soc. chim. 1907, iv. 346; Bouveault and Blanc, Compt. rend. 136, 1903, 167). Identified by the oxime (m.p. 69°), semi-carbazone (m.p. 100°); yields pelargonic acid (b.p. 252°) on oxidation.

n-**Decaldehyde** $C_{10}H_{20}O$, b.p. 93°–94° (12 mm.), 207°–209° (755 mm.), sp.gr. 0·828 at 15°, $n_D^{15°}$ 1·42977 (Stephan, J. pr. Chem. 1900, [ii.] 62, 525). Occurs in orris, neroli, mandarin and other oils. A yield of 52 p.c. is obtained by distilling α-hydroxyundecylic acid. The oxime melts at 69°, semi-carbazone at 102°, β-naphtho-cinchoninic acid compound at 237°.

OLEFINIC TERPENE ALDEHYDES.

Citral (geranial), $C_{10}H_{16}O$

(*a*) $(CH_3)_2C : CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3) : CH{\cdot}CHO$

(*b*) $CH_2 : C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3) : CH{\cdot}CHO$

b.p. 110°–112° (12 mm.); sp.gr. 0·8972 at 15°, n_D 1·4931. Occurs in lemon grass, citronellol, rose, and many other oils, as two stereoisomeric forms (*a*) and (*b*) (chiefly as the former), giving semicarbazones melting respectively at 164° and 171° (Tiemann, Ber. 1899, 32, 115). On oxidising geraniol with chromic acid mixture, a 30–40 p.c. yield of citral is obtained, and it is also formed when linalool and nerol are oxidised. It has been synthesised by distilling a mixture of the calcium salts of geranic and formic acids. On heating with acids, it is converted into cymene (Tiemann, Ber. 1899, 32, 107); with caustic soda, methyl heptenone and acetaldehyde are formed. Oxidation with chromic acid mixture converts it into methyl heptenone, but if first oxidised with cold permanganate and then with chromic acid, acetone and laevulic acid result. In acetic acid solution, it is reduced by sodium amalgam to geraniol. The action of sodium bisulphite produces different compounds according to the conditions (Tiemann, *ibid.* 1898, 31, 3317). The normal compound from which the citral may again be regenerated by the action of alkalis, is formed in the presence of a small quantity of sulphurous acid. The β-naphtho-cinchoninic acid compound (m.p. 200°) is used for its identification.

Citronellal $C_{10}H_{18}O$

$(CH_3)_2C : CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CHO$

$CH_2{:}C(CH_3)CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)CH_2{\cdot}CHO$

b.p. 205°–208°, 103°–105° (25 mm.); sp.gr. 0·8538 at 17·5°, n_D 1·4481, α_D 12° 30′. Occurs chiefly in citronella oil. It is reduced by sodium amalgam to citronellol; the action of acids results in closing the ring, *iso*pulegol being formed. The action of sodium bisulphite has been studied by Tiemann (Ber. 1898, 31, 3305). By adjusting the conditions, methods of separating citral and citronellal have been devised. Thus whilst citral reacts with dilute solutions of sodium bisulphite and bicarbonate, citronellal reacts only with concentrated solutions (Ber. 1899, 32, 815). Much discussion has taken place as to the identity of natural citronellal with the compound obtained by oxidising rose-oil citronellol, the latter compound being designated by Barbier and Bouveault as rhodinal. The conversion of rhodinal to menthone under the influence of acids is affirmed by Barbier and Bouveault (Compt. rend. 1896, 122, 737; 1904, 138, 1699; Bull. Soc. chim. 1900, [iii.] 23, 458), although denied by Tiemann and Schmidt (Ber. 1897, 30, 38).

Harries and Himmelmann (Ber. 1908, 41, 2187) have since shown that in citronellal the two isomeric compounds formulated above are present. The semicarbazone (m.p. 82·5°) and β-naphthyl cinchoninic acid compound (m.p. 225°) are characteristic.

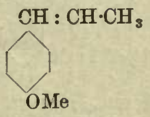
AROMATIC ALDEHYDES.

Benzaldehyde $C_6H_5{\cdot}CHO$ (*v.* BENZALDEHYDE).

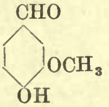
Phenyl acetaldehyde $C_6H_5{\cdot}CH_2{\cdot}CHO$; b.p. 75° (5 mm.), sp.gr. 1·0315 at 15°, $n_D^{20°}$ 1·52536 (Schimmel and Co.). This may be obtained from phenyl chlor (or α-brom) lactic acid or from phenyl and α-brom-styrol. By gentle oxidising agents it is converted into the corresponding acid. It is unstable and tends to polymerise on keeping.

Cinnamaldehyde $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$ (*v.* CINNAMIC ALDEHYDE).

Salicyaldehyde $C_6H_4(OH)CHO$ (*v.* SALICYLIC ALDEHYDE).

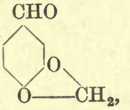
Anisaldehyde $C_6H_4(OCH_3)CHO$, *p*-methoxy benzaldehyde (Aubépine); b.p. 248° (corr.), 91° (4 mm.), sp.gr. 1·126–1·129 at 15°, $n_D^{20°}$ 1·572. Prepared by the oxidation of anise oil, consisting chiefly of anethole  with about 10 p.c. of the isomeric estragole. The oxidising agents used are dilute nitric acid, chromic acid mixture or ozone. It is also obtained by the methylation of *p*-hydroxybenzaldehyde. The semi-carbazone melts at 203°–204°, the two modifications of the oxime at 63° and 132° respectively.

Vanillin

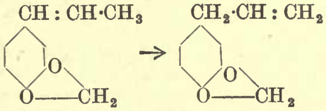


(*v.* VANILLIN).

Heliotropin (Piperonal)



methylene protocatechuic aldehyde. White crystals, m.p. 36°; b.p. 236°. Heliotropin has the characteristic odour of heliotrope flowers, but it has only been detected with certainty in the flowers of *Spiræa ulmaria* (Linn.). It was originally synthesised by Fittig and Mielk from piperonylic acid, and was prepared from piperine. Ground pepper is mixed with slaked lime and water, evaporated to dryness and extracted with ether. The residue is boiled with alcoholic potash and the potassium piperate formed oxidised with permanganate. From the filtered solution, heliotropin crystallises out. It is now manufactured by the oxidation of *iso*safrol with permanganate or chromic acid. The product is steam distilled, extracted with ether and purified by means of its bisulphite compound. The yield produced by oxidation of safrole is much less, so that the safrole is converted first to *iso*safrole by boiling with alcoholic potash.



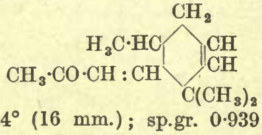
The use of ozone as oxidising agent gives a good yield of a pure product (Otto). It may also be prepared by the action of methylene iodide on protocatechuic aldehyde in presence of alkali.

Since its introduction in 1879, the price has fallen from £150 to 30*s.* per kilo. It must be kept in a cool, dark place since it becomes gradually discoloured on exposure to light; in the hot weather it is conveniently kept in alcoholic solution. It may be identified by a semicarbazone (m.p. 224°–225°), by reduction to piperonyl alcohol (m.p. 51°), or by oxidation to piperonylic acid (m.p. 228°).

KETONES.

The most important members of this class are irone, the odoriferous principle of orris-root ionone, the basis of the synthetic violet perfumes, and jasmone, the ketone isolated by Hesse from jasmine oil, the constitution of which is as yet unknown.

Irone $C_{13}H_{20}O$

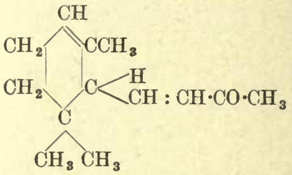


b.p. 144° (16 mm.); sp.gr. 0·939 at 20°, $[\alpha]_D$ +40°, n_D 1·50113 (Tiemann and Kruger).

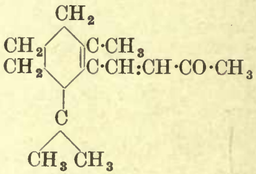
The orris root is extracted with ether and the extracted matter distilled in steam. The volatile fraction contains irone, myristic, and oleic acids and their esters and oleic aldehyde. The acids and esters are removed by treating with alcoholic potash, the aldehydes oxidised by means of silver oxide, and finally the irone separated by conversion into its phenyl hydrazone (Tiemann and Kruger, Ber. 1893, 26, 2675). It may be obtained more conveniently from orris-root oil by fractional distillation. The smell of the pure substance is sharp when concentrated, but if largely diluted, resembles that of violets. Its synthesis has been accomplished by Merling and Welde (Annalen, 1909, 366, 119) who, starting from *iso*propylidene acetoacetic ester, succeeded in obtaining Δ-4-*cyclo*citral; on condensing this with acetone, irone was produced.

It is characterised by a *p*-bromophenyl hydrazone (m.p. 174°–175°), and an oxime (m.p. 121·5°), crystallising with difficulty.

Ionone $C_{13}H_{20}O$



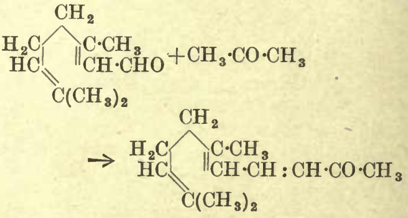
α



β

α-Ionone, b.p. 123°–124° (11 mm.), sp.gr. 0·932 at 20°, n_D 1·4980; β-Ionone, b.p. 127°–128·5° (10 mm.), sp.gr. 0·946 at 17°, $n_D^{17°}$ 1·521.

Ionone, obtained by Tiemann and Krüger (Ber. 1893, 26, 2691) in an unsuccessful endeavour to synthesise irone, forms the basis of synthetic violet perfumes. Citral and acetone interact, in the presence of alkaline condensing agents, forming *pseudo*-ionone, a pale yellow strongly refractive oil, boiling at 143°–145° (12 mm.)



This, when treated with acids, is converted into a mixture of the isomeric cyclic ketones α- and β- ionone. As the alkaline condensing agent dilute baryta water may be used, or the dry mixture of citral and acetone may be shaken with dry sodium peroxide (Kayse, D. R. P. 127661), or with PbO, LaO, or borates (Haarman and Reimer, D. R. P. 130457). The proportion of α- or β- compound produced depends on the nature of the acid chosen to effect the closing of the ring. Concentrated sulphuric acid, or the prolonged action of dilute acids produces chiefly the β- compound, concentrated phosphoric or formic acids almost entirely the α- derivative. α-Ionone is transformed by concentrated sulphuric acid into the β- compound. Various methods have been devised for the separation of the α- and β- forms. If the mixed bisulphite compounds be distilled in steam, β- ionone distils over; the α- compound remains behind in combination and is liberated on the addition of alkali. The difference in solubility of the semicarbazones may also be utilised.

α-Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 142°–143°).

β-Ionone is characterised by a *p*-bromphenyl hydrazone (m.p. 116°–118°).

The semicarbazones melt respectively at 107°–108° (α) and 148° (β).

A large number of patents deal with the preparation of similar products. Homologues of acetone and other ketones may replace acetone (Fr. Pat. 269884). Ivalderine is thus produced by condensing with methyl ethyl ketone, ianthone with methyl pentenone (Fr. Pat. 278333), ganthone with mesityloxide (D. R. P. 118288). Calcium chloride and iron chloride have also been used as condensing agents. The characteristic violet odour of these compounds only becomes apparent in dilute solutions.

Ionone hydrate and its homologues prepared by condensing citral hydrate with acetone are also described (Coulin, D. R. P. 198483, 200654).

LACTONE.

Coumarin (*v.* Coumarin) has the scent characteristic of new mown hay.

OXIDE.

Cineol (*v.* Camphors).

COMPOUNDS CONTAINING NITROGEN.

Indole, a constituent of jasmine flower oil (*v.* Indoles).

Scatole occurs in civet (*v.* Indoles).

Methyl anthranilate, m.p. 24°–25°; b.p. 132° (14 mm.), sp.gr. 1·168 at 15°. Occurs in neroli, tuberose, ylang-ylang, jasmine flower, bergamot and other oils. It consists of white crystals which show a blue fluorescence; solutions are also fluorescent.

Methyl methylanthranilate, m.p. 18·5°–19·5°; b.p. 130° (13 mm.), sp.gr. 1·120 at 15°. Occurs in mandarin oil.

Nitrobenzene is used as a substitute for bitter almond oil.

Trinitro-tert.-butyltoluene

$$(NO_2)_3C_6H(CH_3)C(CH_3)_3$$

(Tonquinol or Musc Baur), pale yellow crystals (m.p. 96°–97°). Prepared by condensing *iso*butyl chloride with toluene in the presence of $AlCl_3$ and nitrating the product formed; during the process, the *iso*butyl is transformed to tertiary butyl. The butyl toluene is added to 5 times its weight of a mixture of 1 part HNO_3 (1·5) and 2 parts fuming H_2SO_4 containing 15 p.c. anhydride and heated at 100° for 8–9 hours.

THE USE OF SYNTHETIC SUBSTANCES IN THE BLENDING OF PERFUMES.

By suitably mixing and diluting the compounds enumerated above, a great variety of perfumes may be produced and many of the natural oils and extracts imitated. The exact composition of these substitutes varies with the particular maker and is kept as a trade secret. As far as possible, a knowledge of the composition of the natural oil serves as a guide in choosing the constituents; in the blending of perfumes the best results appear to be obtained by the addition of both natural and synthetic products. Thus, in the group of perfumes, jasmine, lilac, muguet, &c., jasmine oil is added to a mixture of synthetic substances.

Bergamot. The natural oil contains about 38 p.c. of linalyl acetate: other constituents are limonene, di-pentene, linalool, camphene, octylene, acetic acid (Burgess and Page, Chem. Soc. Trans. 1904, 85, 1327), and two substances of unknown constitution, bergaptene

$$C_{11}H_5O_3{\cdot}OCH_3$$

(Pomeranz) and bergaptine, a coumarin-like substance, melting at 59·5° (Soden and Rojahn, Pharm. Zeit. 46, 778). The main constituent of the synthetic oil is linalyl acetate; terpineol acetate, geranyl propionate, and geranyl methyl ether are also used in its preparation.

Carnation. Eugenol, *iso*eugenol, caryophyllene are used as ingredients of oil of carnation.

Hawthorn. The scent of the hawthorn is faithfully reproduced by anisaldehyde (Aubépine).

Heliotrope. Attempts to identify heliotropin in the extract of heliotrope flowers have failed; the odour of synthetic heliotropin closely resembles that of the heliotrope flower and is the basis of all the heliotrope perfumes. Its odour is improved by the addition of coumarin and vanillin and by blending with rose or jasmine oil.

Hyacinth. Enklaar (Chem. Weekblad, 1, 1910, 7) identified benzyl alcohol, benzyl benzoate, and ethyl cinnamate in the essential oil of hyacinth; he failed to detect methyl anthranilate. Cinnamic alcohol is especially characterised by a hyacinth-like smell. The following constituents are used in preparing an oil of hyacinth: phenyl ethyl alcohol, cinnamic alcohol, phenyl ethyl aldehyde, methyl benzoate, phenyl ethyl acetate, methyl and ethyl cinnamates, terpineol, and α-chlor- and α-bromstyrolenes.

Jasmine. The oil extracted from the pomade obtained from jasmine flowers by the process of enfleurage was shown by Hesse to have the following composition (Ber. 1899, 32, 2611).

Benzyl acetate . .	65·0	p.c.
Linalyl acetate . .	7·5	,,
Benzyl alcohol . .	6·0	,,
Linalool . . .	16·0	,,
Indole	2·5	,,
Methyl anthranilate .	0·5	,,
Jasmone (a ketone $C_{11}H_{16}O$)	3·0	,,

The methyl anthranilate cannot be extracted directly from the plant, but appears to be formed during the process of enfleurage. By distillation with steam, 0·4 p.c. methyl anthranilate was obtained. The oil obtained by distilling the fresh flowers was found to be free from indole (Hesse, Ber. 1904, 37, 1457).

Elze (Chem. Zeit. 1910, 34, 912) found, in addition to the above, cinnamyl acetate, geraniol, *p*-cresol, and *p*-cresyl methyl ether. The synthetic oil consists chiefly of benzyl acetate and benzyl alcohol to which cinnamic acetate, linalool and its acetate, indole and methyl anthranilate may be added. The substance peculiarly characteristic of the jasmine scent appears to be the ketone jasmone, which cannot yet be obtained synthetically. A proportion of jasmine oil is generally added to the mixture of synthetic substances, as the oil prepared only from synthetic substances is not entirely satisfactory.

Lilac. Terpineol is the characteristic constituent of lilac perfumes. Commercial terpineol is prepared by the action of dilute acids on terpin hydrate, the fraction boiling up to 216°, being known as terpinol and terpinolene, above 216° as terpineol. Commercial terpineol is obtainable both in the solid and liquid forms, the latter having the more intense odour. It contains both di-pentene and terpinolene.

Lily of the Valley (**Muguet**). Terpineol is also used as a constituent of the lily of the valley perfumes with geraniol and citronellol. A mixture of 90 p.c. terpineol and 10 p.c. palma rosa oil has a strong muguet odour. Linalool, benzyl alcohol and its acetate are amongst the other constituents employed.

Musk. Natural musk, obtained from an abdominal gland of the musk deer (*Moschus moschiferus*), owes its characteristic odour to a ketone, muscone ($C_{15}H_{30}O$ or $C_{15}H_{28}O$); the distillate obtained on distilling the secretion in steam is extracted with ether, treated with alcoholic potash, washed with water and finally distilled *in vacuô*. The ketone passes over in the fraction boiling at 145°–147° (3 mm.). Muscone is now sold in alcoholic solution. As early as 1759, Margraff had obtained a product smelling of musk by treating amber with nitric acid. In 1878, von Gerichten observed the musk-like odour of chlor- and brom-nitro-cymenes and three years later, Kolbe prepared another musk-scented compound, di-nitro-*m*-cymene. In 1888, Baur took out the first patents for the preparation of artificial musk and has since made an exhaustive study of the groups in the benzene ring conditioning the musk-like odour. Two nitro- groups must be present, and a third negative group symmetrically arranged; the three other positions are filled by alkyl groups, of which one must be a tertiary radicle. A large number of these artificial musks, di-nitro- or tri-nitro- derivatives of tert-butyl-toluene or -xylene, have been introduced. The most important of these are:

Musc Baur	Trinitro-tert-butyltoluene
Moschus .	
Tonquinol .	
	Trinitro tertiary-butylxylene
Musk ketone	Dinitro-tert-butyl-*m*-xylyl methyl ketone
Musk aldehyde	Dinitro-butyl-*m*-xylyl aldehyde

Orange-flower (synthetic neroli oil). The composition of a specimen of the natural oil is given as follows (Hesse and Zeitschel, J. pr. Chem. 1902, [ii.] 66, 481):—

	p.c.
Hydrocarbons (pinene, camphene, dipentene and a paraffin C_{27})	35·0
Terpene alcohols and acetates—	
l-Linalool	30·0
l-Linalyl acetate	7·0
d-Terpineol	2·0
Geraniol and nerol	4·0
Geranyl and neryl acetates	4·0
d-Nerolidol	6·0
Methyl anthranilate	0·6
Acetic and palmitic acids	0·1
Indole	0·1
Resin and loss (decylic, phenyl acetic acids, &c.)	11·2
	100·0

Methyl and ethyl β-naphthyl ethers are employed as substitutes for neroli oil; a mixture of the two was originally introduced as nerolin, the former is now known as yara-yara, the latter as bromelia. In the composition of the synthetic oil, geraniol, linalool, nerol, and their acetates with methyl anthranilate are used. A solution of 40 grams of the synthetic oil in 1 kg. of alcohol constitutes the tincture used as the equivalent of the first infusion of the flower pomade.

Rose. The natural oil was shown by Markownikoff in 1891 (Ber. 23, 3191) to consist of an inodorous hydrocarbon, stearoptene, melting at 36·5° and a liquid portion, eleoptene, from which two substances, having the composition $C_{10}H_{18}O$ and $C_{10}H_{20}O$, could be separated. In the same year, Poleck and Eckart (*ibid.* 23, 3554) showed that the liquid constituent $C_{10}H_{18}O$ (rhodinol) was identical with geraniol, isolated by Semmler from Indian geranium oil and constituting 66–74 p.c. of German and 80–88 p.c. of Turkish rose oil. The presence of citronellol ($C_{10}H_{20}O$) was established by Tiemann (Ber. 29, 921), who, by treating the alcohols at a low temperature with PCl_3 in ethereal solution, obtained a phosphite of citronellol, geranyl chloride remaining in the ethereal solution. These two alcohols form the main constituents of rose oil and of such preparations as roseol, reuniol, &c. In 1900, it was shown that the extract of fresh rose-leaves contained about 2 p.c. of phenyl ethyl alcohol. This was present to a much less extent in the oils obtained by steam distillation, owing probably to the loss of the sparingly soluble alcohol in the steam distillate. In addition to the above alcohols, small amounts of linalool, citral, and nonaldehyde were detected (Walbaum, Ber. 1900, 33, 2299, 2302; *cp.* Soden and Rojahn, *ibid.* 1900, 33, 3063; Schimmel, Rep. 1900, 53). The substances enumerated above are used in the manufacture of synthetic rose oil. Up to the present, the scent of the oil prepared entirely from synthetic substances cannot rival the fragrance of the natural product. The most successful preparations contain some proportion of the natural oil or of the tincture made from the natural extract, to which some synthetic rose oil and such substances as neroli oil, vanillin, musk, or other synthetic compounds may be added at the discretion of the perfumer. Extensive adulteration of the natural oil takes place at the source of production, *e.g.* in Bulgaria, the geraniol and citronellol from cheaper oils, such as geranium, palma rosa, being added and distilled with the rose oil.

Violet. The basis of the artificial violet perfumes is ionone or some closely allied substance. The scent of α-ionone is stated to be sweeter and more penetrating, resembling more closely that of orris root; that of the β-compound resembles more closely the natural violet. After smelling a natural violet extract or a solution of ionone for some little time, the odour often cannot be perceived, the nasal nerve-endings being easily fatigued by this scent. The smell of violets is only apparent when the pure substance is diluted. Ionone was originally placed on the market as a 10 p.c. alcoholic solution, 10 grams of which gave 1 kilogram of violet tincture. Now the pure substances, consisting of 100 p.c. α-ionone and 100 p.c. β-ionone respectively are obtainable. Irone and derivatives of ionone also find application. With the violet tincture so prepared, other tinctures made both from natural and synthetic oils are blended: rose, jasmine, orris, ylang-ylang, are amongst those thus used. As instances of violet scents prepared from natural and synthetic substances, the following may be quoted (Mann, Moderne Parfumerie):—

Spring violet. grms.		Violet scent. grms.		
6000	Infusion violets, I.	5000	Tincture ionone	Synthetic
2000	,, rose, I.	1000	,, rose-oil	
750	,, jasmine, I	1000	,, jasmine	
250	,, acacia	300	,, orange	
50	Tincture coumarin	3000	,, iris oil	
50	Infusion benzoin	50	,, musk	
50	,, musk	10	Ylang-ylang oil	
100	Solution rose oil	200	Infusion benzoin	
100	Tincture vanillin			
40	,, viodoron			

Ylang-ylang oil. The oil extracted from the flowers of *Cananga odorata* (Hook.) (*v.* OILS, ESSENTIAL) contains about 30–32 p.c. linalool, 9 p.c. linalyl benzoate, 7 p.c. linalyl acetate, a little geraniol, and about 30 p.c. of a hydrocarbon, cadinene. Methyl alcohol and *p*-cresyl acetate have also been detected (Darzens, Bull. Soc. chim. 1902, 27, 83). Bacon identified in addition formic acid and *iso*safrol (Schimmel, Rep., Oct. 1908). In the composition of the artificial oil, the following compounds occur; linalool, geraniol, methyl and ethyl benzoates, linalyl and geranyl benzoates, benzyl salicylates and other esters. Bacon (*l.c.*) also examined a number of esters with reference to their suitability as constituents of this oil.

New mown hay. Coumarin forms the main constituent of this perfume and with it tinctures of orange, rose, jasmine, &c., are blended.

As instances of two well-known fancy perfumes, the following may be quoted (Mann, Moderne Parfumerie). These are, of course, subject to wide variation.

Peau d'Espague. grms.		Ess bouquet. grms.	
50	Cassie flower oil	2000	Tincture of rose, I.
100	Sandalwood oil	1000	,, cassie, I.
60	Niobe oil	1000	,, tuberose, I.
200	Bergamot oil	2550	Extract of reseda
1000	Tincture of musk	2000	,, bergamot
1500	,, civet	10	Rosewood oil
1000	Infusion of tolu	50	Bergamot oil
40	Vetiver oil	100	Infusion of musk, I.
10	Turan oil	50	Tincture of civet
10,000	Spirit	100	Infusion of tolu
		3	Turan oil

Eau de Cologne. This, one of the oldest and most famous of perfumes, was manufactured in Cologne at the end of the seventeenth century. It is disputed whether Johann Maria Farina or Paul de Feminis of Milan, both of whom came from Italy to Cologne, was the original inventor; in both cases the secret was bequeathed to their successors, that of Paul de Feminis passing to his nephew, Johann Anton Farina: there are now three firms bearing the name Farina who claim to possess the original formula and who zealously guard it. The general nature of the preparation of Eau de Cologne is, however, known, although details of the preparation may be lacking. The quality of the spirit used is of paramount importance: only the most highly purified spirits of wine may be used, and after the perfume is prepared, it must be left for a long time, some years if possible, to mature. The firms who possess the original secret continue to use the same ingredients and are not concerned with synthetic oils. Other perfumers make use of such synthetic oils as nerol and bergamot, with those of rosemary, lemon, lavender, and petit-grain; the composition of each Eau de Cologne varies considerably. A typical example is as follows:—

30,000 grams spirit.
100 ,, neroli oil.
30 ,, rosemary oil.
100 ,, Mitcham lavender oil.
300 ,, lemon oil.
300 ,, bergamot oil.
50 ,, petit grain oil.

(*See* OILS, ESSENTIAL; Gildemeister und Hoffmann, Die Aetherischen Oele, 1910, Otto, Les Parfums; Mann, Die Moderne Parfumerie; &c.) I. S.

PERHYDROL. Trade name for a solution of hydrogen peroxide (*q.v.*).

PERICLINE *v.* FELSPAR.

PERILLA OIL. Perilla oil occurs to an extent of 35·8 p.c. in the nuts of *Perilla ocymoides* (Linn.), an annual labiate, indigenous to the East Indies as also to China (Manchuria) and Japan. It is extensively grown in China and Japan, and is also cultivated in the Himalayas. The plant is sown in April, blossoms about the end of September, and ripens two weeks later. The seed is known in Japan as Ye-Goma, or Se-no-abura. For the physical and chemical characteristics, *see* tables under OILS, FIXED, AND FATS.

This oil has the highest iodine value of any known fatty oil, and simulates linseed oil in taste and smell. Endeavours have been made to import it into Europe as a substitute for linseed oil. J. L.

PERMANGANATES *v.* MANGANESE.

PERNAMBUCO WOOD *v.* BRAZIL WOOD.

PEROFSKITE or **PEROVSKITE** *v.* TITANIUM.

PERONIN. Trade name for the hydrochloride of morphine benzyl ester, used as a sedative (*v.* SYNTHETIC DRUGS).

PEROXOLS. Trade names for mixtures of hydrogen peroxide containing salicylic acid, carbolic acid, β-naphthol, thymol, camphor, menthol, &c. Used as disinfectants.

PEROXYDASES *v.* Fermentation.

PERSEITOL *v.* Carbohydrates.

PERSIAN BERRIES are the seed-bearing fruit of various species of *Rhamnus*, growing wild or cultivated in France, Spain, Italy, the Levant, and Persia. The Persian berry proper is obtained from *R. amygdalinus*, *R. oleoides*, and *R. saxatilis*, and is imported from Smyrna and Aleppo. Its size is about that of a pea, colour yellowish-green, surface much shrivelled, hard, and divisible along well-marked depressions forming a cross, into four parts, each containing a triangular seed; its taste is intensely bitter.

Avignon or French berries, the product of *R. infectorius* (Linn.) and *R. Alaternus* (Linn.), are smaller in size than the foregoing and contain only two seeds.

Spanish, Italian, and Hungarian berries are respectively the products of *R. saxatilis*, *R. infectorius* (Linn.), and *R. cathartica* (Linn). These are similar in quality to the Avignon berries. Other qualities come from the Morea, Wallachia, and Bessarabia.

That all of these botanical varieties do not contain the same constituents appears certain from the work of Tschirch and Polacco (Arch. Pharm. 1900, 238, 459) and other chemists, on the *R. cathartica*; but, on the other hand, there is every reason to suppose that the colouring constituents of the botanical group to which the term Persian berry proper is applied are identical in each case.

Gelatly (Edinburgh New. Phil. Jour. 7, 252) was the first to isolate from Persian berries (*R. tinctoria* [Wald. et Kit.]) the glucoside *xanthorhamnin* $C_{45}H_{56}O_{28}$, which on hydrolysis with acid gave a sugar and a colouring matter *rhamnetin*. Hlasiwetz (Annalen, 112, 107) considered that xanthorhamnin was identical with quercitrin, and rhamnetin with quercetin, but Schützenberger and Bertèche (Bull. Soc. Ind. Mulhouse, 35, 456) denied this, and assigned to rhamnetin the formula $C_{12}H_{10}O_5$. Xanthorhamnin, which Schützenberger (J. 1868, 774) termed *α-rhamnegin* was considered to possess the formula $C_{24}H_{32}O_{14}$. The presence of a second glucoside, *β-rhamnegin* was also detected by this chemist, and from this by hydrolysis *β-rhamnetin* was derived. Liebermann and Hörmann (Annalen, 196, 313) also investigated Persian berries, devised a method for the preparation of xanthorhamnin and rhamnetin, and prepared various derivatives of the latter.

It is now known that Persian berries contain the glucosides of three colouring matters, namely rhamnetin, rhamnazin, and quercetin (Herzig, Monatsh. 6, 889; 9, 549; 12, 175; Perkin and Geldard, Chem. Soc. Trans. 1895, 67, 500).

To isolate these substances Persian berries are extracted with boiling water, the solution treated with a small quantity of sulphuric acid, and digested while boiling for one hour. The glucosides are thus hydrolysed and the crude colouring matters separate in the form of a greenish-yellow precipitate.

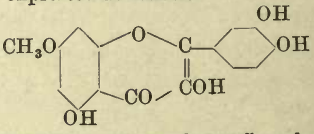
The product is extracted with boiling alcohol, which dissolves principally the *quercetin*, this being the most soluble of the three colouring matters. The residue now contains rhamnetin and rhamnazin, and the latter is removed from the former by two or three extractions with boiling acetic acid.

Rhamnetin $C_{16}H_{12}O_7$ crystallises in yellow needles very sparingly soluble in acetic acid and alcohol. It dissolves in alkaline solutions with a pale yellow colour, and gives with alcoholic lead acetate an orange-red precipitate. When acetylated it forms *tetra-acetyl rhamnetin* $C_{16}H_8O_7(C_2H_3O)_4$ (Liebermann and Hörmann), colourless needles, m.p. 183°–185°, and on bromination *dibromrhamnetin* is produced.

Rhamnetin sulphate $C_{16}H_{12}O_7,H_2SO_4$ (Perkin and Pate, Chem. Soc. Trans. 1895, 67, 650), orange-red needles, and *monopotassium rhamnetin* $C_{16}H_{11}O_7K$ (Perkin and Wilson, *ibid.* 1903, 83, 136), orange-yellow needles, have been prepared.

Rhamnetin is in reality a *quercetinmonomethyl ether* (Herzig, *l.c.*), for on digestion with hydriodic acid it is converted into *quercetin*, and when methylated with methyl iodide *quercetintetramethyl ether* is produced.

By the action of boiling potassium hydroxide solution, of boiling alcoholic potash, or by aspirating air through its alkaline solution, rhamnetin gives *protocatechuic acid*, and a syrupy phloroglucinol derivative. The latter, identified by means of its diazobenzene compound, consists of *phloroglucinol monomethyl ether* (Perkin and Alleson, Chem. Soc. Trans. 1902, 81, [illegible]70), and consequently the constitution of rhamnetin is to be expressed as follows:



Rhamnetin is a strong dyestuff, and gives on mordanted woollen cloth shades which are practically identical with those produced by quercetin:

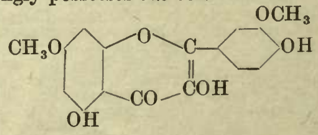
Chromium.	*Aluminum.*	*Tin*	*Iron.*
Red brown.	Brown orange.	Bright orange.	Deep-olive.

(Perkin and Wilkinson, *ibid.* 1902, 81, 590).

Rhamnazin $C_{17}H_{14}O_7$ (P. and G.), yellow needles, m.p. 214°–215°, is moderately soluble in boiling toluene, a property which distinguishes it from both rhamnetin and quercetin. It dissolves in alkaline liquids to form orange-yellow solutions, and with alcoholic ferric chloride gives an olive-green colouration.

Acetyl rhamnazin $C_{17}H_{11}O_7(C_2H_3O)_3$, colourless needles, *benzoylrhamnazin* $C_{17}H_{11}O_7(C_7H_5O)_3$ colourless needles, m.p. 204°–205°, and dibromorhamnazin $C_{17}H_{12}Br_2O_7$, yellow needles have been prepared.

Rhamnazin is a *quercetin dimethyl ether*. Digested with boiling hydriodic acid, it is converted into quercetin, and by means of methyl iodide into quercetin tetramethyl ether. Boiling alcoholic potash hydrolyses rhamnazin with formation of *vanillic acid* and *phloroglucinol monomethyl ether* (Perkin and Allison, *l.c.*). It accordingly possesses the constitution—



Rhamnazin does not readily dye mordanted calico, but on mordanted wool gives shades resembling those which are produced by kaempferol—

Chromium.	*Aluminum.*	*Tin.*	*Iron.*
Golden yellow.	Orange yellow.	Lemon yellow.	Olive brown.

Only a small amount of this colouring matter is present in Persian berries.

Xanthorhamnin $C_{34}H_{42}O_{20}$ is readily prepared by extracting powdered Persian berries with three times their weight of boiling 85 p.c. alcohol. On standing the dark brown filtered extract deposits a large quantity of the impure glucoside as a brown resinous mass. From the supernatant liquid on standing a purer xanthorhamnin separates in the form of pale yellow cauliflower-like precipitate, and in such quantity as to congeal the whole liquid to a stiff paste. This is collected, repeatedly crystallised from alcohol, and finally from alcohol containing a little water and ether (Liebermann and Hörmann, *l.c.*).

Xanthorhamnin consists of pale-yellow needles readily soluble in water and hot alcohol, soluble in alkaline solutions with a yellow colour. With basic lead acetate it gives an orange precipitate. According to the work of Liebermann and Hörmann, xanthorhamnin, when hydrolysed with acid, gives *rhamnetin* and *rhamnose*

$$C_{48}H_{66}O_{29}+5H_2O=4C_6H_{14}O_6+C_{12}H_{10}O_5.$$

More recently, however, xanthorhamnin has been shown to possess the formula $C_{34}H_{42}O_{20}$, and that by means of its specific ferment *rhamninase*, contained by Persian berries, it is hydrolysed with formation of rhamnetin and a complex sugar *rhamninose* $C_{18}H_{32}O_{14}$

$$C_{34}H_{42}O_{20}+H_2O=C_{16}H_{12}O_7+C_{18}H_{32}O_{14}.$$

When rhamninose is digested with boiling dilute acids, it is converted into 2 molecules of *rhamnose*, and 1 molecule of *galactose* (C. and G. Tanret, Compt. rend. 1899, 129, 725)

$$C_{18}H_{32}O_{14}+4H_2O=C_6H_{12}O_6+2C_6H_{14}O_6.$$

No glucosides of rhamnazin or quercetin have been isolated as yet from Persian berries. The action of the ferment rhamninase is readily demonstrated. If crushed Persian berries contained in a muslin bag, are suspended in water heated to 40°, a yellow solution containing the glucosides is produced; this quickly becomes opaque and a heavy precipitate of the mixed colouring matters is eventually produced. To within recent years this reaction was carried out on a commercial scale, and the product was placed on the market under the name of 'rhamnétine.' This reaction can be employed to distinguish between the dyeing properties of the glucosides contained in the berries, and the free colouring matters produced by their hydrolysis. Thus if Persian berries be added to a cold dyebath, and this is slowly heated to boiling, the glucosides are hydrolysed by the ferment; but if, on the other hand, the berries be at once plunged into boiling water, the ferment is killed and a solution of the glucosides is obtained. In the former case wool mordanted with tin gives an orange-red shade, whereas in the latter a pure yellow colour is produced.

Beyond the ordinary extract of Persian berries which is prepared in large quantity by extracting the berries with boiling water, and evaporating the solution under reduced pressure, no special commercial preparations are manufactured at the present time.

Dyeing properties.—In wool dyeing Persian berries are little employed on account of their expensive nature; moreover, they possess no special advantage over quercitron bark and old fustic. Persian berries, as a rule, give redder shades than quercitron bark, a fact which is to be explained as due to the hydrolysis of its glucosides by the ferment. The quercitrin of quercitron bark is not accompanied by such a specific ferment, and consequently the shades given by this dyestuff are of a yellower character. With tin mordant Persian berries give bright yellows and oranges, which are only fairly fast to light; but according to Hummel, the yellowish-olive produced with copper mordant is extremely fast, and is darkened rather than otherwise by exposure. Persian berries are still used to a considerable extent in calico-printing for the formation of yellow, orange, and green shades.

A. G. P.

PERSIAN GREEN. *Emerald green v.* PIGMENTS.

PERSIAN RED. *Basic lead chromate v.* CHROMIUM.

PERSIMMON, the fruit of *Diospyros virginiana* (Linn.), much cultivated in Japan, and now in California and other warm countries. When freshly gathered, the fruit has a very astringent taste, which it loses on keeping, especially if exposed to a low temperature.

König gives as its average composition—

Water	Protein	Invert sugar	Cane sugar	Other N-free extract	Fibre	Ash
66·1	0·8	13·5	1·0	16·0	1·8	0·9

Tannin is abundant in the freshly gathered fruit, but on storage is deposited in an insoluble form, in certain specialised cells (Bigelow, Gore and Howard, J. Amer. Chem. Soc. 1906, 28, 688).

H. I.

PERSULPHURIC ACID and PERSULPHATES *v.* SULPHUR.

PERTHITE *v.* FELSPAR.

PERU BALSAM *v.* BALSAMS.

PERUVIAN BARK *v.* VEGETO-ALKALOIDS.

PERYLENE (*peri*-dinaphthylene). A hydrocarbon $C_{20}H_{12}$ obtained by heating either naphthalene, or 1 : 1′-dinaphthyl with aluminium chloride; or by heating 1 : 8-di-iodonaphthalene with finely divided copper. Glistening yellow crystalline leaflets, m.p. 264°–265°, forming yellow to reddish-yellow solutions with a blue fluorescence (Scholl, Seer and Weitzenböck, Ber. 1910, 43, 2202).

PETALITE. A lithium aluminium silicate $LiAl(Si_2O_5)_2$ containing 4·9 p.c. lithia, and much resembling spodumene [$LiAl(SiO_3)_2$] in appearance. It usually forms platy, cleavable masses (hence the name, from πέταλον, a leaf) of a white, grey, or pinkish colour and with a vitreous lustre; sp.gr. 2·4 (that of spodumene being 3·16). It is found, together with other lithium-bearing minerals (lepidolite, tourmaline, and spodumene), in an iron mine on the island of Utö near Stockholm, where it has been mined as a source of lithium salts. It was in this mineral that lithium was discovered by J. A. Arfvedson in 1817. Other localities are Peru in

Maine, and Bolton in Massachusetts. A colourless, glassy variety, known as castorite, is found in the granite of the island of Elba. L. J. S.

PETIT-GRAIN OIL *v.* OILS, ESSENTIAL.

PETROFRACTEUR. An explosive resembling *kinetite* (*v.* EXPLOSIVES) in composition, but differing specially in that it contains no guncotton. Is said to consist of a mixture of 10 p.c. nitrobenzene, 67 p.c. potassium chlorate, 20 p.c. potassium nitrate, and 3 p.c. antimony pentasulphide (*v.* Watson Smith, J. Soc. Chem. Ind. 1887, 5).

PETROLEUM.

AMERICAN PETROLEUM.

I. *Occurrence.*

Three closely-related raw materials, all belonging to the class of bitumens, have been noted as occurring associated together, sometimes as distinct occurrences, sometimes in complete physical admixture, viz. natural gas, liquid petroleum, and ozokerite or natural paraffin. To these three must be added, in considering the American production, a fourth variety of bitumen, asphalt, for we have learned to speak of petroleums with a paraffin base and petroleums with an asphaltic base, from which latter variety much true asphalt can be and is now industrially obtained.

Leaving this distinction between native petroleums to be referred to more fully in speaking of the ultimate products and utilisations, we will note the present production of crude petroleums in America. The producing fields are now commonly grouped under eight heads: (*a*) the Appalachian field, (*b*) the Lima-Indiana field, (*c*) the Illinois field, (*d*) the Mid-continent field, (*e*) the Gulf field, (*f*) the California field, (*g*) other fields of the United States, (*h*) Canadian field.

The Appalachian field. Under this head is now included the production of Pennsylvania, New York, Eastern Ohio, West Virginia, Kentucky and Tennessee, which states lie along the Appalachian range. In general, the oil is what is known as 'Pennsylvania' grade, and commands a higher price than any other. This is because it contains a paraffin base, is practically free from sulphur compounds, and, in consequence, is more readily refined and yields a higher percentage of valuable products. In certain parts of this field very valuable natural lubricating oils are obtained, and in some amorphous paraffin separates out in the tanks used for storage of the crude oil and in the pipelines. Because this petroleum is so largely made up of the paraffin series of hydrocarbons, it is easily refined by acid treatment and yields the largest proportion of gasoline and burning oil. It is true that the Kentucky and Tennessee oils are not quite equal to the Pennsylvania grade, but they are nevertheless of the same paraffin-base class of oils. Of the states comprising the Appalachian field, West Virginia now leads, with Pennsylvania second, and south-eastern Ohio third. In general this grade of crude oil is gathered by the pipe-lines under collective names of Bradford crude in the northern part, Middle-District crude for the central, and South-Western crude for the West Virginia and South-Eastern Ohio oil.

The Lima-Indiana field. This takes its name primarily from the town of Lima in Northern Ohio where this class of oil was first produced. It does not come from a sandstone formation as in the case of the Appalachian oil, but from what is known geologically as the Trenton limestone, in which alteration of the dolomitic limestone has left porosity sufficient for considerable oil accumulations. This oil, as that from the neighbouring state of Indiana, is sulphur containing, and therefore more difficult and expensive to refine. It, however, contains a paraffin base, and is now made to yield products nearly or quite equal to those obtained from Pennsylvania oil.

The Illinois field. This is of relatively recent development, only having begun to produce actively in 1906, but in 1909, it ranked third in amount of production, being exceeded only by California and the mid-continent fields. It now exceeds the entire Appalachian field in its production.

The oil is in the main found in the sandstone formation, and hence is geologically different from the Lima-Indiana oil, and contains less sulphur. It is also a paraffin-base oil, and as far as examined chemically it seems to stand intermediate between the Pennsylvania oils and the Lima-Indiana oil.

Mid-Continent field. The area included in this field consists of southern Kansas, the oil deposits of the new state of Oklahoma (formerly Indian territory), and northern Texas. This field is also of comparatively recent development, having developed from less than one million barrels in 1902 to about fifty million barrels in 1909, and 53,500,000 barrels in 1910, so that it is only exceeded in production at present by the California field. By far the largest amount of the oil is produced in Oklahoma, Kansas coming second. The oil is most generally of a somewhat asphaltic base, although paraffin-containing oil is obtained from part of the field. Very much of the oil from this field is now used as fuel oil and has been extensively introduced in place of coal, so that the production of the latter has fallen off in several of the states supplied by pipe-line from the Oklahoma oil regions.

The Gulf field. This includes the oil fields of Louisiana and coastal Texas. In this field, the accumulation of petroleum is determined by a type of geologic structure which is unique. The oil occurs in recent rocks and these formations are characterised by flat or gently sloping strata, in which occur peculiar domes. These latter are perhaps uplifts, perhaps due to subterranean crystallisation of salt, gypsum and limestone, which may have elevated the strata above them so as to form these characteristic domes or 'mounds,' as they are called. Drilling on the top or sides of these mounds has frequently developed, as at Spindle-Top, large oil gushers associated with salt water. Most of the Texas oil is mainly valuable for fuel oil, because of the low percentage of burning-oil fraction obtainable and the presence of heavy hydrocarbons. It, moreover, is largely of an asphaltic base, and therefore the residuums from Texas oils have been of especial value for fluxing the hard asphalts. The Beaumont oil is one of the strongest in sulphur of American petroleums and the sulphur compounds are of an unstable character so that free sulphur at times deposits

C H

from them, as was first established by Richardson, and in their distillation much hydrogen sulphide is liberated.

The California field. This field, since 1909, has become the first in amount of production, having furnished in that year the enormous yield of 58,250,300 barrels, and in 1910 the still larger production of nearly 78,000,000 barrels.

The California production is moreover practically all obtained from four or five contiguous counties in southern California, partly coastal and partly forming the valleys between the Sierras and the Coast Range. Kern and Fresno counties, which lie inland, are at present the most prolific sections, the noted Coalinga deposit being in the latter county, while Santa Barbara, Ventura, and Los Angeles counties, which are coastal counties, are next in importance. The California oil sands have been found to be of much greater thickness than those of eastern fields. In some instances 1100 feet of oil sand has been encountered in a well and in hundreds of wells from 200 to 500 feet of sand are found. This insures a long life to the individual wells. While there is some variation in the California oils, they are in general distinguished by two characteristics: they almost all contain nitrogen, indicating in part at least an animal origin, and they contain an asphaltic rather than a paraffin base. Indeed, they are found associated with solid asphalt deposits and much of the residuum from California oil is used as asphaltic flux and for the manufacture of artificial asphalt. Much of the California oil is used as fuel oil, and enormous quantities are taken for this purpose by the railroads and steamship lines.

Other fields of the United States. Only two additional states require special mention in this connection, Colorado and Wyoming. Colorado for a number of years has produced a moderate amount of an oil with a paraffin base and free from sulphur, the production being centred in two localities, Florence and Boulder. Wyoming produces an oil, also free from sulphur, and especially characterised by the excellent quality of the lubricating fraction so that it has commanded a special price.

II. *Physical and Chemical Properties.*

The petroleums of North America as now known differ very widely in both physical and chemical characters. When the American petroleum industry began in 1861, and for many years thereafter, the oil that was refined and marketed was Pennsylvania crude, or as it is now called, Appalachian oil. This, as already stated, is relatively easily refined and yields a large percentage of excellent quality burning oil and paraffin, and is substantially free from sulphur and nitrogen. Later the Lima, Ohio oil, and the Canadian oils were discovered, which contained a smaller percentage of illuminants and notable amounts of sulphur compounds and required a special and more expensive refining treatment. They, however, contained a paraffin base. The California oil, however, was of notably different type, much of it was very heavy, some being found of a density as low as 12°B., and it yielded very little illuminating oil. It was soon found to contain, in addition to sulphur, organic nitrogen compounds, and the hydrocarbons present were not of the paraffin series, which were so characteristic of Pennsylvania oil, but heavy asphaltic oils which, on concentration, yielded solid asphalt material.

The Texas oil, which next appeared, seems in large degree to be intermediate between these types, and while yielding some paraffin contains also much asphaltic base. It is also specially characterised in some localities by an abundance of loosely-combined and even free sulphur. The Illinois field, as already stated, is more an approximation to the Appalachian field, yielding a paraffin-base oil, although with more sulphur than Pennsylvania oil, while the Mid-Continent field, on the other hand, yields predominantly an asphaltic-base oil, although yielding paraffin in many cases.

The crude petroleums vary in colour and gravity from the dense California oils, which are almost black, to the light crudes, of 51°B. in parts of the Appalachian field, which are greenish in bulk and reddish-brown by transmitted light, or exceptionally yellow or amber in colour.

Scientific study of American petroleums has been made chiefly by Warren, C. F. Mabery, Clifford Richardson, and Young.

Besides the saturated paraffin series

$$C_nH_{2n+2},$$

which constitutes the bulk of the Pennsylvania oil, unsaturated open-chain hydrocarbons, probably of the series C_nH_{2n} are found. The well-known aromatic series C_nH_{2n-6} also occurs in many of the paraffin-base oils of Pennsylvania and Ohio, and in the asphaltic oil of California, but not, so far as known, in the Canadian oil or the Texas oils.

Saturated hydrocarbons of the series C_nH_{2n-2} and C_nH_{2n-4} (therefore cyclic and not open-chain hydrocarbons) have been recognised by both Mabery and Richardson as present in the heavier fractions of many oils both of the Pennsylvania and the California type.

Unsaturated cyclic hydrocarbons of high molecular weight are found to be the characteristic constituents of asphalt-base oils like those of California.

The sulphur compounds of the Lima and the Canadian oils are now believed by Mabery to be cyclic in character and polymethylene derivatives. He terms them thiophanes. The nitrogen compounds of the California oils are basic bodies, and are supposed to be pyridine and quinoline derivatives.

Phenolic bodies have also been recognised in the California petroleums, and have been extracted in crystalline form by Richardson.

III. *Production and Transportation of the Crude Petroleum.*

The oil comes from depths which vary within very wide limits according to the geological formations, from the heavy oil strata of West Virginia and Ohio, which are from 50 to 60 feet deep, to the producing strata of the Washington Co., Pennsylvania district, which are from 2400 to 2600 feet in depth, and to some of the California wells, where, as in the Santa Maria district, wells have been drilled to a depth of over 4000 feet. Many wells, particularly in newly-opened territory, where the original gas-pressure has not been lost, are flowing wells, known among oilmen as 'gushers.' This yield, however, is never long maintained, and declines rapidly until pumping becomes necessary in order to maintain the production of oil. The American oil wells have in general never equalled the prolific yield of some of the Baku oil-fountains. The bulk of the production in the American fields is only obtained as the result of systematic pumping. There are exceptions, however, to this rule. The famous Lake-view gusher in Kern Co., California, has probably not been equalled in the history of the petroleum industry of the world. It was brought in, in March, 1910, at a rate estimated at 10,000 barrels a day, later increasing its capacity to about 30,000 barrels. Occasionally it placed to its credit 60,000 barrels during a single day. After about nine months of steady flowing it collapsed, as a result of salt water breaking into the oil sand. During its career, it was estimated to have produced over 8,000,000 barrels of oil, or more than one-tenth of the total output of the state.

The oil comes usually from well-defined strata of conglomerate, or 'sand-rocks,' which are separated by slate or shale rock. These 'oil-sands' occur frequently in groups of three, as the Venango first, second, and third sands; the Warren sands; and the Bradford sands. These sands occur at intervals as we go deeper, beginning with the newest geologically, and going down to the older groups. It may happen, too, that in a particular locality the upper sand of a group yields the oil (in which case it is likely to be of a heavier character), and in another locality this sand may be barren, while oil is yielded by a lower one. It is rare, however, to find an abundance of oil in several sand rocks of the same geological group.

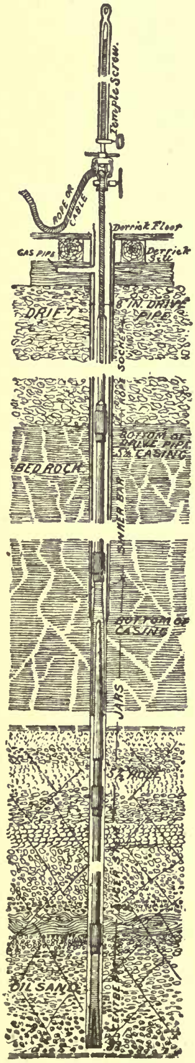


FIG. 1.

This article will not allow of a detailed description of the extremely ingenious apparatus now used in boring the American oil-wells, and in fitting them for the production of oil. The accompanying illustration gives a sectional view of the drilling of such a well, and the several strata penetrated (Crew on Petroleum, p. 192).

'Torpedoes,' or charges of nitro-glycerin, have been used in the Pennsylvania and the Canadian fields in order to shatter the oil-sand and open up communication with new portions of the spongy and oil-saturated stratum. The charge in the former locality often rises to 80 or even 100 quarts of nitroglycerin, and in the Canadian field to the tenth part of this amount. The main torpedo is fired by the use of a miniature torpedo or 'squib' which is run down in contact with the other, and then fired by dropping a weight upon it.

The transportation of crude oil from the wells, which are often in isolated positions, to centrally located storage tanks, and from the points of production to the refineries, is now effected almost exclusively by means of pipe-lines. And as it was found more convenient to locate the great refineries on the Atlantic seaboard, or in large manufacturing centres, the pipe-lines were in time extended so that New York, Philadelphia, Baltimore, Pittsburg, Cleveland, and Buffalo are all connected now with the oil-producing regions of Pennsylvania and New York by long lines of pipe. These great trunk lines, 6 inches in diameter, thus traverse nearly the whole length of the two great States of New York and Pennsylvania, and deliver thousands of barrels of oil daily to refineries on the route and at their different termini on the seaboard. The six great lines referred to as running to the main refining centres are owned by the National Transit Company, an organisation closely connected with the Standard Oil Trust. The New York division consists of two 6-inch pipe-lines, extending from Olean, N.Y., to Bayonne, N.J., and Hunter's Point, N.Y., 312·6 miles in length, with eleven pumping stations for this distance, and has a capacity of 28,000 barrels per diem. The pipes are buried at a depth of two or three feet, and follow the general contour of the country through which they pass. The pumps, generally of the Worthington pattern, are powerful machines, and, in order to force the oil such great distances against the friction of the pipes, carry a pressure of from 1200 to 1500 lbs. to the square inch. The pipes on the main line are all tested to a pressure of 2000 lbs. to the square inch. The storage tanks, of which there are two or more at each station, are built of boiler-iron, and hold 35,000 barrels each.

In 1905, immediately upon the discovery of the Mid-Continent field, the Standard Oil Co. pushed its pipe-lines south-westerly 550 miles into Kansas and Oklahoma, and, as this did not relieve the great production of this field, in 1909 great trunk lines were run from the Oklahoma field 500 miles south-easterly to Baton Rouge, Louisiana, where the oil was either refined or shipped by water to all desired points. The new Illinois field was similarly drained by pipe-lines northward to Chicago and westward to the Mississippi. Many large refineries were built in the Central West and along the Gulf to work up as much as possible of this oil. California has three 8-inch trunk pipe-lines carrying the oil from the producing localities to tide-water on San Francisco bay and elsewhere.

The foreign exportation is chiefly of refined oil and other products. A considerable quantity of crude petroleum, however, is exported from the United States to France to be refined there, the French duty on the refined oil encouraging the home refining.

The shipment of refined oil for the Far East is chiefly in cans of tin, two of which latter, holding five gallons American, or nearly four imperial gallons each, are packed together in a wooden case. These cases go to China, Japan, and warm climates, as the loss by leakage is less than when the barrel is used. The shipment of oil in bulk for the voyage across the Atlantic to Europe is now carried on most largely in tank steamers, and quite a fleet run from Philadelphia and New York to English and German ports. The most important feature of their construction is the provision of auxiliary tanks above the level of the main storage tanks and in communication with them. The storage tanks can thus always be kept full of oil, the auxiliary tanks serving to hold the surplus when the storage tanks become heated and supplying the deficiency when contraction takes place.

IV. *Processes of Refining and Manufacture.*

As petroleum has been shown to be a mixture of hydrocarbons of different volatility, the first operation would naturally be to effect a partial separation of these hydrocarbons by a process of fractional distillation. But, in fact, simpler lines of treatment were first tried. It was found that crude oils spread out over warm water in tanks and exposed to the sun were much improved in gravity and consistency. This process was chiefly employed for the production of lubricating oils, and the products were called 'sunned oils.' This was followed by the application of methods of partial evaporation or concentration in stills, either by direct application of heat or by the use of steam-coils, carefully avoiding over-heating. The products were called 'reduced oils,' and form the best material for the manufacture of high-grade lubricating oils. They will be referred to again. The process to which the great bulk of crude petroleum is submitted, however, is that of fractional distillation, continued to the eventual coking of the residue. As the most valuable of the several distillates is that which is to be used as illuminating oil, the percentage of that distillate obtainable is an important item in an oil refinery. A normally conducted fractional distillation of Pennsylvania petroleum will give from 35 to 50 p.c. of oil suitable for illuminating purposes, and from 20 to 30 p.c. of lubricating oils. About 1865, however, it was found that if during the distillation the heavy vapours were made to drop back upon the hot oil in the still they became superheated and were decomposed. This process of destructive distillation or 'cracking' allowed of a notable increase of the illuminating oil fraction at the expense of the lubricating oil. So, at present, some 75–80 p.c. of burning oil is obtained, whilst the residuum from which the lubricating oil is obtained is reduced to 6 p.c.

The process of refining crude petroleum is generally divided into two quite distinct parts. The 'benzine' and burning oil distillate are run from the same still, when the fluid residuum is transferred to what are usually called 'tar stills,' in which the rest of the distilling operation is conducted. The crude-oil stills in almost exclusive use at present, consist of a cylinder of boiler-plate, the lower half being generally of steel, 30 feet in length by 12 feet 6 inches in diameter. This still is set horizontally in a furnace of brickwork usually so constructed that the upper half of the still is exposed to the air, which facilitates the cracking in the latter part of the distillation. The working charge of the cylinder stills is usually 750 barrels, although 1000 barrels stills are often used. The stills are usually provided with steam pipes both closed and perforated. The steam issuing in jets from the perforated pipe has been found to facilitate distillation by carrying over mechanically the oil vapours.

The condensing apparatus varies somewhat in the details of its construction, but consists essentially of long coils of pipe immersed in tanks through which water is kept flowing. The terminal portions of the condensing pipes all converge and enter the receiving house within a few inches of each other. Near the extremity of each a trap in the pipe is made for the purpose of carrying away the uncondensable vapour. This may be allowed to escape or may be burned underneath the boilers or stills, effecting thereby a large saving in fuel. The condensing pipes generally deliver into box-like receptacles with plate-glass sides, through which the running of the distillate can be observed, and from which test portions can be taken from time to time for the proper control of the process.

The tar-stills are usually of steel, cylindrical in shape, holding about 260 barrels, and are set in groups of two or more, surrounded by brick-work. Vacuum-stills have been and are still used to some extent, especially in the preparation of reduced oils, for the manufacture of lubricants and products like vaseline. Of course, the evaporation in these stills takes place rapidly, and at the lowest temperature possible, insuring a fractional distillation and not a decomposition. If superheated steam be used, moreover, instead of direct firing, it is possible to reduce oils to 18°B. without any production of pyrogenic products. Continuous distillation has not proved commercially successful in the United States, but has latterly been taken up again and is used on certain kinds of crude oil.

To recur now to the products of the first rough distillation of crude oil, the first fraction, known as the 'benzine distillate,' is redistilled by steam heat in cylindrical stills holding 500 barrels, and is sometimes separated into the following products: cymogen, 100°–110°B. gravity; rhigolene, 90°–100°B.; gasolene, 80°–90°B.; naphtha, 70°–76° B.; benzine, 62°B. gravity. The time occupied in working the charge is about 48 hours. The deodorisation of the benzine, which is to be used for solvent purposes in pharmacy or the arts, is effected by the use of sulphuric acid, as in the treatment of the burning oil fraction, only the proportion of acid used is much smaller, and the agitation is effected by revolving paddles instead of by an air-blast. One-half of 1 p.c. is sufficient in this case. Other processes have been proposed for the deodorisation, such as the method of the United States Pharmacopœia for 'purified benzine,' which is to agitate the benzine first with dilute sulphuric acid to which potassium permanganate has been added, and then with sodium hydroxide solution to which a similar addition of potassium permanganate has been made, and followed finally by washing with water.

The treatment of the illuminating oil fraction is a more important process. It is first subjected to treatment with sulphuric acid, washing with water and a solution of caustic soda. This operation is conducted in tall cylindrical tanks of wrought iron, lined with sheet lead, which are called 'agitators.' The bottom is funnel-shaped, terminating in a pipe furnished with a stop-cock for drawing off the refuse acid and soda washings. The distillate to be treated must be cooled to at least 60°F., and before the main body of the acid is added for the treatment any water present must be carefully withdrawn. This is done by starting the agitation of the oil by the air-pump and introducing a small quantity of acid. This is allowed to settle and withdrawn. The oil is now agitated and about one-half of the charge of acid is introduced gradually from above. The agitation is now to be continued as long as action is indicated by rise of temperature, when the dark 'sludge acid' is allowed to settle and withdrawn. The remaining portion of the acid is added and a second thorough agitation takes place. The whole charge of acid needed for an average distillate is about 1½–2 p.c., or about 6 lbs. of acid to the barrel of oil. The acid as drawn off is dark-blue or reddish-brown in colour, and is charged with the sulpho- compounds of the olefines and other unsaturated hydrocarbons. while the free sulphur dioxide escapes in abundance. The oil, after treatment, consists of the paraffin hydrocarbons largely freed from admixture with olefines and other hydrocarbons. In colour it has been changed from brownish-yellow to a very light straw shade. The oil is now washed with water introduced through a perforated pipe running round the upper circumference of the tank. This water percolates through the body of the oil, removes the acid, and is allowed to escape in a constant stream from the bottom.

When the wash-water shows no appreciable acid taste or reaction the washing is stopped and about 1 p.c. of a caustic soda solution of 12°B. is introduced and the oil is again agitated. When this is drawn off the oil is ready for the settling tanks. Washing with water after the soda treatment sometimes follows, but is not general. The settling tanks are shallow tanks, exposed to air and light on the sides, and in these any water contained in the oil settles out and the oil becomes clear and brilliant. The tanks are provided with steam coils for gently warming the oil in cold weather to facilitate this separation. The bringing of the burning oil fractions to proper fire-test is now always accomplished by 'steam-stilling,' or taking out the light vapours until test is reached. These light vapours are of course condensed and go into the gasolene tank.

In the refining of the Canadian oil which contains sulphur impurities, after the caustic soda washing, the oil has been treated with a solution of litharge in caustic soda, agitation being continued for about 6 hours, or until the oil is deodorised. Sublimed sulphur is then added and the agitation renewed. After the first drawing off of the litharge solution the oil is bleached in sunlight. The oil, however, is not freed from all its sulphur impurity, even by this elaborate treatment. More recently it has been found that distillation over finely-divided metallic copper under certain conditions will much more effectually free these oils from the sulphur, and this method has been extensively used in refining Lima Ohio oil.

The residuum of the original crude oil distillation is, as was said, distilled from the 'tar stills.' The first runnings, constituting from 20 to 25 p.c., will have a gravity of 38°B., and are returned to the crude-oil tank for distillation or are treated and purified as burning oil. The paraffin oil which now runs over may be caught in separate lots, as it deepens in colour and increases in density, or it may be all received together to be treated in the paraffin agitator with acid and purified for the separation of paraffin wax. The agitator in this case must be provided with steam pipes so that its contents can be kept perfectly liquid, and the charge of acid is larger, amounting to 3, 4, or even 5 p.c. The treatment included the usual washing with water and soda, all at the proper temperature. The 'sludge' becomes quite solid on standing, and is not worked over. After settling, the paraffin oil goes to the chill rooms, where, by the aid of the ammonia-refrigerating machines and the circulation of cooled brine, the whole mass is brought to a semi-solid condition. This is filter-pressed at low temperatures, and the refined heavy oil which drains off is collected as lubricating oil. The press-cake may be broken up, melted, and recrystallised, and then submitted to still greater pressure at a higher temperature (70°F.) than before, when it is known as 'refined wax.' To convert it into block paraffin it must be washed with benzine, pressed, melted, and filtered through selected filtering clay, when it is obtained perfectly colourless and solidifying to a hard translucent block.

The distillation of residuum is continued until the bottom of the still becomes red hot, when yellow vapours issue from the tail-pipe and a dense resinous product of a light yellow colour and nearly solid consistency distils over. This 'yellow wax' contains anthracene and other higher pyrogenic hydrocarbons. Its only use at present is to add it to paraffin oil to increase density and lower cold tests. The coke remaining in the still amounts to about 12 p.c. Reduced oils, obtained by careful driving off of the light fractions of the crude petroleum without cracking, as stated before, are of great value as lubricants. They are generally made by vacuum distillation, and the use of superheated steam instead of direct firing. They are either brought into the market at once without further treatment or after a bone-black or clay filtration. This production of filtered oils is usually combined with the manufacture of vaseline or 'petrolatum,' as it is now known in the U. S. Pharmacopœia. Taking a vacuum residuum as the raw material, this is melted and run on to filters of fine granular well-dried bone-black. The filters are either steam-jacketed or are placed in rooms heated by steam coils to 120°F.

or higher. The first runnings are colourless; and all up to a certain grade of colour go to the manufacture of vaseline. Beyond that the filtrate is known as 'filtered cylinder oil,' and is used as lubricant exclusively.

The process of filtration of oils through fuller's earth, now extensively practised with lubricating oils and paraffin, has also been applied in an experimental way by Dr. David T. Day, of the U.S. Geological Survey to crude petroleums with interesting results, showing not only a decolourising effect, but in addition a fractionation. These results are briefly summarised thus (Bulletin, 365, U.S. Geological Survey): '1. When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom. 2. When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards when more water is added. 3. When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffin hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom. 4. When oil is mixed with fuller's earth and then displaced with water, about one-third of the oil remains in the earth.' These results are interesting, as throwing light upon the occurrences of different grades of crude oil under different geological conditions.

There are several relatively new lines of manufacture of petroleum products that also require special mention.

The great demand for gasoline for automobile, motor-boat, and manufacturing processes has caused petroleum refiners to turn to all possible sources of these light fractions. Normally 100 barrels of crude yield but 5–7 barrels of a good quality gasolene, and the consumption of gasolene has now risen to 200,000,000 gallons per year. Much attention has therefore been given to obtaining a light gasolene by condensing the heavier portions of natural gas, especially what is termed 'casing-head gas.' In West Virginia and south-eastern Ohio several plants have been started for condensing from this gas its liquefiable portions. Gas-pumps are in use for drawing from petroleum wells the heavier portions of the petroleum gas, much of which is condensable. In California large quantities of heavy petroleum gas are also obtained, and it is stated that every 1000 feet of the gas will yield, on condensation, two gallons of gasolene. As thousands of irrigating plants are driven by gasolene engines, and many gas motors are in use for all kinds of work, the demand for gasolene has made this new source a very welcome one.

Gas oils are now produced very extensively from such crude oils as Texas petroleum, which do not yield large percentages of kerosene, and are then destructively distilled in gas-making. The oil-gas thus obtained has a high illuminating power, and is mixed with water-gas, which, although cheap, has no illuminating value unless carburetted.

Petroleum residuums, notably the Lima residuum and latterly the Mid-Continent oil residuums, are blown with a current of air, while kept at a temperature below their distilling-point, with the result of the formation of a semi-solid or solid product resembling asphalt and used at present extensively as a flux for the hard natural asphalts. The California petroleum readily yields an asphaltic residue when distilled and much artificial asphalt for paving purposes is made in this state. Sulphur, when heated with the liquid California petroleums of asphaltic base, also causes a thickening and the production of a solid asphaltic flux.

V. *Character of Products and Utilisations.*

The names of commercial products obtained from petroleum have, of course, been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally accepted classes of products. The first fraction commercially obtained is the 'light naphtha.' From this may be obtained by special fractioning and proper condensation :—

Cymogene, gaseous at ordinary temperatures, but liquefiable by cold or pressure, b.p. 0°C., sp.gr. 110°B. Used in the manufacture of ice.

Rhigolene, condensable by the use of ice and salt, b.p. 18·3°C., sp.gr. 0·60 or 100°B. Used as an anæsthetic for medical purposes.

Light Petroleum or *Petroleum ether* (Sherwood oil), b.p. 70°–90°C., sp.gr. 0·650–0·666 or 85°–80°B. Used as a solvent for caoutchouc, asphalts, and fatty oils, and for carburetting air in gas machines.

The light petroleum used by chemists for solvent purposes may be very light, 88°B., or may be as heavy as 62°B., which latter is used in certain classes of extraction.

Ligroin is another name for light petroleum.

Benzine (deodorised), sp.gr. 0·638–0·660 at 25°C. (82°–89°B.), boiling at 45°–60°C., is the light solvent described in the U.S. Pharmacopœia.

Gasoline. This term is now broadly applied to the product used for automobiles, motor-boats, and internal-combustion engines, and because of its demand may vary quite widely in quality. Moreover, as gasoline is made now not only from Pennsylvania oil, but from oils like California and Mid-Continent, which are differently constituted chemically, the products will differ quite notably in physical characters. Thus a California naphtha of 66°B. gravity will evaporate at ordinary temperatures much more readily than Pennsylvania gasoline reading 80°B. or higher. Or again a well-made 60°–63° gravity naphtha, manufactured from Mid-Continent crude, has a lower b.p. than 76° gravity naphtha made from Pennsylvania crude.

In general, commercial gasolines are of heavier gravity than before the demand grew to its present figures.

Burning oil or kerosene. The different burning oils are known often by special names, of which the number is legion, but they are graded by the American petroleum exporters, chiefly according to the two standards of colour and fire-test, the colours ranging from pale-yellow (standard-white) to straw (prime-white), and colourless (water-white). The fire-tests to which the commercial oils are mostly brought are 110°F., 120°F., and 150°F., that of 110° going mainly to the Continent of Europe and to China and Japan, and that of 120° to England.

Most of the kerosene for export is now refined on the basis of the Abel test. An oil of 150°F. fire-test and water-white in colour is known in the trade as 'head-light oil.' An oil of 300° fire-test, and sp.gr. 0·829 is known as 'mineral sperm' or 'mineral-colza' oil.

Lubricating oils from petroleum have assumed an importance which is increasing every year. Some crude petroleums like those of Franklin and Smith's Ferry, Pennsylvania, Mecca, Ohio, Volcano, W. Virginia, and other localities, are natural lubricating oils, requiring little or no treatment to fit them for use. The other petroleum lubricating oils are prepared in one of two ways—either by driving off the light hydrocarbons from the crude oil, yielding what is called a 'reduced oil,' or they are the oils obtained by distilling the petroleum residuum in tar-stills. The lightest of the lubricating oils, varying in gravity from 32°B. to 38°B., are frequently called 'neutral oils.' They are largely used for the purpose of mixing with animal or vegetable oils, and it is therefore necessary that they should be thoroughly deodorised, decolourised, and deprived of the blue fluorescence or 'bloom.' The first two results are accomplished by bone-black filtration, the last in various ways, such as treatment with nitric acid, addition of small quantities of nitronaphthalenes, &c.

Heavier lubricating oils are called 'spindle' and 'cylinder' oils. S. P. S.

PETROLEUM FROM OTHER SOURCES THAN AMERICA.

Towards the close of the nineteenth century the United States and Russia occupied positions of greater importance in respect of the present and prospective supplies of petroleum than is now the case, for within recent years there has been great activity in the exploration of petroliferous regions and the exploitation of other sources of supply, with the result that, although the United States furnishes considerably more than half the aggregate output, many other countries are now contributing on a scale of increasing commercial importance, and the production of petroleum has become widespread in character.

In these circumstances it is desirable to give statistics of the world's output of petroleum for 1911, the latest year for which official returns are obtainable, before proceeding to supplement the account of the petroleum industry in the United States by particulars of the corresponding industry in other countries (see top of next column).

WORLD'S PRODUCTION OF CRUDE PETROLEUM IN 1911.
(Day.)

Source.	Metric Tons.	Percentage of Total.
United States	29,393,252	63·80
Russia	9,066,259	19·16
Mexico	1,873,522	4·07
Dutch East Indies	1,670,668	3·52
Roumania	1,544,072	3·21
Galicia	1,458,275	3·04
India	897,184	1·87
Japan	221,187	0·48
Peru	186,405	0·40
Germany	140,000	0·29
Canada	38,813	0·08
Italy	10,000	0·02
Other Countries*	26,667	0·06
	46,526,334	100·00

* Estimated.

Russia.

There can be little doubt that the so-called Eternal Fires at Surakhani, on the Apsheron peninsula, have been frequented by fire-worshippers since the commencement of the Zoroastrian period, to which the date of 600 B.C. has usually been assigned, although the temple which now stands in that locality is considered to be of Hindu origin, and is probably not more than two centuries old.[1] In Gibbon's 'Decline and Fall of the Roman Empire' it is recorded that Heraclius, having, in A.D. 624, wintered in the Mogan Steppes, at the mouth of the river Kura, 70 miles south of Baku, 'signalised the zeal and revenge of a Christian Emperor. At his command, the soldiers extinguished the fire and destroyed the temple of the Magi.'

Marco Polo, writing in the thirteenth century, says, 'On the confines towards Georgine, there is a fountain from which oil springs in great abundance, inasmuch as a hundred shiploads might be taken from it at one time. This oil is not good to use with food, but 'tis good to burn, and is also used to anoint camels that have the mange. People come from vast distances to fetch it, for in all the countries round there is no other oil.'[1] With reference to this, Colonel Yule remarks, 'Though Mr. Khanikoff (the celebrated Russian traveller) points out that springs of naphtha are abundant in the vicinity of Tiflis, the mention of shiploads (in Ramusis, indeed, altered—probably by the editor—to camel-loads) and the vast quantities spoken of, point to the naphtha wells of the Baku peninsula on the Caspian. Ricold speaks of their supplying the whole country as far as Bagdad, and Barbaro speaks of their practice of anointing camels with oil.' Peter the Great, upon annexing Baku in 1723, made arrangements for the collection of the oil and its transportation up the Volga. A few years later, Baku having meanwhile been restored to Persia, attempts were made by England to establish a trade with India *viâ* the Caspian Sea, and, some complications having arisen, Mr. Jonas Hanway was deputed to proceed to Persia to investigate affairs. Upon his return Mr. Hanway published, in 1754, An Account of British Trade over the Caspian Sea, wherein the following references to petroleum occur: 'What the Guebers, or Fire-worshippers, call the Everlasting Fire, is a phenomenon of a very extraordinary nature. This object of devotion lies about ten English miles north-east by east from the City of Baku, on a dry rocky land. There are several ancient temples built with stone, supposed to have been all dedicated to fire. Amongst others is a little temple at which the Indians now worship. Here are generally forty or fifty of these poor devotees, who come on a pilgrimage from their own country. A little way from the temple is a low cleft of a rock, in which there is a horizontal gap, two feet from the ground, nearly six long, and about three broad, out of which issues a constant flame, in colour and gentleness not unlike a lamp that burns with spirits, only more pure. When the wind blows it rises sometimes eight feet high, but much lower in still weather. They do not perceive that the flame makes any impression on the rock. This also the Indians worship, and say it cannot be resisted, but if extinguished will rise in another place. The earth round the place, for above two miles, has this surprising property, that by taking up two or three inches of the surface and applying a live coal the part which is so uncovered immediately takes fire, almost before the coal touches the earth; the flame makes the oil hot, but does not consume it, nor affect what is near it with any degree of heat. Any quantity of this earth carried to another place does not produce this effect. Not long since eight horses were consumed by this fire, being under a roof where the surface of the ground was turned up, and by some accident took flame. If a cane or tube, even of paper, be set about two inches in the ground, confined and closed with earth below, and the top of it touched with a live coal, and blown upon, immediately a flame issues without hurting either the cane or paper, provided the edges be covered with clay; and this method they use for light in their houses, which have only the earth for the floor. Three or four of these lighted canes will boil water in a pot, and thus they dress their victuals. The flame may be extinguished in the same manner as that of spirits of wine. The ground is dry and stony, and the more stony any particular part is, the stronger and clearer is the flame; it smells sulphurous, like naphtha, but not very offensive. Lime is burnt to great perfection by means of this phenomenon, the flame communicating itself to any distance where the earth is uncovered to receive it. The stones must be laid on one another, and in three days the lime is completed. Near this place brimstone is dug, and naphtha springs are found. Baku supplies Ghilan and Mazanderan and other countries contiguous with naphtha.' Hanway adds that 'the chief place for the black or dark-grey naphtha' was 'the small island Wetoy, now uninhabited, except at such times as they take naphtha from thence.' The island thus referred to is Sviatoi or Holy Island, which lies at the extremity of the peninsula of Apsheron. Of the Wetoy naphtha Hanway says, 'The Persians load it in bulk in their wretched vessels, so that sometimes the sea is covered with it for leagues together. When the weather is thick and hazy, the springs boil up the higher, and the naphtha often takes fire on the surface of the earth, and runs in a flame into the sea in great quantities, to a distance almost incredible. In clear weather the springs do not boil up above two or three feet; in boiling over the oily substance makes so strong a consistency as by degrees to almost close the mouth of the spring. Sometimes it is quite closed, and forms hillocks that look as black as pitch, but the spring which is resisted in one place breaks out in another. Some of the springs which have not been long open form a mouth of eight or ten feet diameter. The people carry the naphtha by troughs into pits or reservoirs, drawing it off from one to another, leaving in the first reservoir the water or the heavier part with which it is mixed when it issues from the spring. It is unpleasant to the smell, and used mostly among the poorer sort of the Persians and other neighbouring people, as we use oil in lamps, or to boil their victuals; but it communicates a disagreeable taste. They find it burns best with a small admixture of ashes. As they obtain it in great abundance, every family is well supplied. They keep it at a small distance from their houses, in earthen vessels underground, to prevent any accident from fire, of which it is extremely susceptible.' Hanway also describes a 'white' variety of naphtha, collected on the peninsula of Apsheron, as 'of a much thinner consistency than black naphtha. The Russians drink it both as a cordial and medicine; but it does not intoxicate. If taken internally it is said to be good for the stone, as also for disorders of the breast, and in venereal cases and sore heads; to both the last the Persians are very subject. Externally applied, it is of great use in scorbutic pains, gouts, cramps, &c., but it must be put to the part affected only; it penetrates instantaneously into the blood, and is apt, for a short time, to produce great pain. It has also the property of spirits of wine to take out greasy spots in silks or woollens, but the remedy is worse than the disease, for it leaves an abominable odour. They say it is carried into India as a great rarity, and being prepared as a japan is the most beautiful and lasting of any that has yet been found.' A third source of petroleum mentioned by Hanway is the island of Tcheleken on the eastern side of the Caspian. Of this island, on which at the present time great activity prevails in petroleum-prospecting, Captain Woodroffe says, 'We weighed, and came in close under the east side of Naphtonia, as the Russians call it. The Persians call it Cherriken. The coast is difficult of access, being high. It contains about thirty-six families who have twenty-eight large boats, with several wells of naphtha. The people exist entirely by piracy. To remedy this evil Nadir Shah, some years ago, offered to forgive all that was past, and to receive them into his favour, if they would come and settle about Astrabad Bay, where they might have lands and sell their naphtha to the inhabitants of that quarter. This they accepted, and carried on a brisk trade for about two years, selling their naphtha to the Persians, Turkomans, &c.; but, getting tired of this way of living, returned to their trade of piracy.'

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[1] When the present writer visited Baku in 1884, he found this temple deserted, and the fires extinguished, but he had no difficulty in igniting the gas.

[1] The Book of Ser Marco Polo, the Venetian. Edited by Colonel Henry Yule, C.B., London, 1871.

Russia again annexed Baku in 1806, and the monopoly of producing petroleum was conferred on a merchant of the name of Mirzoeff, who held it until 1872, when the monopoly was revoked and a tax imposed.

The abolition of the monopoly had the effect of greatly increasing the production, and Mirzoeff did not long retain a position of supremacy, for in 1873 the Khalify Company struck a flowing well which yielded a large supply;

and in the following year the Transcaspian Trading Company, afterwards called the Baku Petroleum Company, took the lead in the business. In 1875 Messrs. Nobel Brothers commenced the systematic production, refining and transportation of petroleum upon a large scale, and by the introduction of approved appliances for drilling and refining, as well as by the installation of a complete system of pipelines, tank steamers, tank barges, tank railroad waggons, and storage tanks, inaugurated a new era in the Russian petroleum industry.

For many years these operations were confined to a few square miles in the Baku district, the producing fields including Balakhani, Sabuntchi, Romani, and Bibi-Eibat, but within this small area such prolific wells were drilled that a very large production was obtained. Thus the celebrated Droojba fountain, completed in 1883, commenced spouting at the rate of 1,600,000 to 2,000,000 gallons daily, valued at £11,000, and other wells drilled within later years have had for a time a daily yield of more than double that quantity.

In 1893 the Grozni field, which lies about 300 miles north-west of Baku, began to attract attention, and two years later it gave so productive a fountain that the outflowing oil converted a neighbouring valley into a vast lake in which large ships could have floated. From that time the progress of Grozni was rapid, and it now ranks as one of the great oilfields of Russia.

The oilfield of Maikop, in which a large amount of English capital has already been expended in drilling operations, is situated in the Kouban territory, about 300 miles west of Grozni. The early promise of large production from moderate depth given by the completion of prolific spouting wells has not been fulfilled, but deep test-wells are being drilled. Meanwhile, however, a steady yield is being obtained from certain parts of the field. Other petroliferous lands lie still further to the north-west on the Taman Peninsula.

As already mentioned, the Island of Tcheleken, on the eastern side of the Caspian Sea, is now being actively exploited with the drill, and spouting wells have been obtained. Ozokerite is also being obtained here in commercial quantity.

Another district in which spouting wells have recently been obtained by drilling is that of Gurieff, in the province of Uralsk, on the northern side of the Caspian Sea.

The cable system of drilling, commonly employed in the United States, which has already been described, has not found favour in Russia, although it has been used. The method adopted is, however, substantially similar, in the sense that the strata are perforated by rapidly successive blows of a steel bit, or cutting chisel, suspended from the end of an oscillating beam, but the drilling tools are attached to the beam by a string of screw-jointed iron rods, added to as the depth of the well increases, instead of being suspended by a Manilla cable, as in America. As the drilling progresses, the detritus is, from time to time, removed from the bore-hole by means of a long cylindrical vessel with a foot-valve, as in the American system. The well is also similarly lined with iron casing, but, owing to the large diameter, riveted casing is used in place of screwed artesian casing. The greater diameter of the Russian wells is due to the need for providing for the use of a bailer (valved cylinder) for raising the oil when the well does not flow, the oil containing so much sand that pumps cannot be used. To some extent the air-lift system of raising the oil has been substituted for bailing within recent years. Motive power for the drilling machinery is ordinarily supplied by a steam-engine, and it is customary to take the steam supply from a central generating station, but the internal combustion engine is also employed, and the use of electricity as a motive power is growing. The oil is transported to the refineries by means of pipe-lines, as in America, and is to some extent stored in similar iron or steel cylindrical tanks of large size, but earthen storage reservoirs are also largely used.

In the refining of the crude oil it is the practice to adopt the system of continuous distillation, which consists in causing the oil to flow through a connected series of horizontal stills heated to successively higher temperatures, each still being provided with a separate condenser, so that a series of distillates of progressively higher boiling-points is simultaneously obtained. In this respect the process of fractional distillation differs from that adopted in America. In the treatment of Baku petroleum the refiner aims at obtaining the largest yield of the ostatki, or residuum, for which there is a large sale as liquid fuel, the kerosene being a product of secondary importance, though a certain proportion of the residuum is further distilled for the manufacture of lubricating oils, as in America. The 'cracking' process, largely employed in the United States as a means of increasing the yield of kerosene, is not adopted in Russia, and in this respect also the procedure in the two countries differs. The yield of kerosene from the crude oil of the older Russian fields does not usually exceed 25–30 p.c., and in the manufacture of the lubricating oils there are no solid hydrocarbons to be separated in the form of paraffin wax, as in America; but oils are now being met with in the newer Russian fields which not only contain a far larger proportion of the more volatile hydrocarbons, but also a considerable percentage of solid hydrocarbons.

The crude petroleum of the Baku district has a specific gravity usually within the limits of 0·855 and 0·875. It is of dark-brown colour and not unpleasant odour. In chemical composition it differs from Pennsylvania and other United States oils in largely consisting of hydrocarbons of the C_nH_{2n} series, which belong not to the ethylene group, but to what is known as the naphthene, or $C_nH_{2n-6}+H_6$, group.

The yield of benzine from the oil of the Balakhani-Sabuntchi field is very small, but a larger proportion of this product is obtained from the Bibi-Eibat oil. The kerosene ordinarily has a specific gravity of about 0·825, which is considerably higher than that of the parallel United States product. Of residuum (ostatki), or fuel oil, with a specific gravity of about 0·912, the yield is from 50 to 60 p.c. The flash-point of this fuel oil is about 140°F., and its calorific value is 10,800 calories, or

19,440 B.T.U. The comparatively small proportion of the residuum which is subjected to further distillation for the manufacture of lubricating oils yields first an intermediate product, known as solar oil, which is largely used as a source of gas for illuminating purposes. About 30 p.c. of the residuum is represented by a machine oil of a specific gravity of about 0·908, and of fairly high viscosity, which is an excellent lubricant for general use.

The crude petroleum of the Grozni field is of higher specific gravity than that of the Baku region, but contains a larger proportion of the more volatile constituents.

For consumption in Russia the kerosene is conveyed from the Baku refineries in bulk by tank-steamers to the mouth of the Volga, and thence by tank-barges and railway tank-waggons. For shipment abroad the kerosene was formerly transported to Batoum by railway tank-waggons, but within recent years a pipeline for the conveyance of it to the Black Sea has been in operation.

Austria-Hungary.

Galicia. The petroleum industry of Galicia is one of considerable antiquity, for the oldest historical records show that the oil was collected for use as cartgrease from very early times, and as a medicinal agent Galician petroleum was held in high repute, under the name of 'earth balsam,' as far back as 1506. In 1810, or between that year and 1818, oil from the Drohobycz district is said to have been distilled by Hecker and Mitis in a small refinery at Kabicza, and the product is reported to have been used for lighting the Alstettering in Prague. Refining does not, however, appear to have been generally practised until 1852, when a manufacturer of cartgrease named Schreiner took some of the liquid condensed on the cover of a vessel in which he had heated the crude oil to an apothecary of the name of Mikolasch, whose assistants, Lukasiewicz and Zeh, treated the distillate with sulphuric acid and caustic soda, and obtained a burning oil of such excellence that renewed attention was directed to the subject. In the following year Galician petroleum replaced candles for lighting the station of the Emperor Ferdinand's North Railway, and in 1854 it obtained a footing as an article of commerce in Vienna.

The Galician oil-deposits extend for a length of about 220 miles, with a width of 40 to 60 miles, in a general north-westerly and south-easterly direction along the northern slopes of the Carpathian mountains. The unexploited deposits in Bukowina and in Transylvania, and the highly important and rapidly developing oil-fields of Roumania, occupying the south-eastern and southern slopes of the Southern Carpathians or Transylvanian Alps, may be regarded as an extension of the Galician deposits.

The earliest systematic exploitation of the petroliferous lands of Galicia was commenced in 1854 in the Bobrka district, between Krosno and Dukla; but the wells were merely shallow hand-dug shafts, which yielded no great quantity of oil, and it was not until many years later, when drilling by steam-power was adopted, that the production assumed commercial importance. To Messrs. Bergheim and MacGarvey the credit is due of having laid the foundation of the present Galician petroleum industry by the introduction of the Canadian system of drilling in the year 1882. This system, which differs mainly from what is known as the American system in the use of wooden rods instead of a cable for the suspension of the drilling tools, was found as suitable for Galicia as it had proved to be for Canada, and for many years the only alteration made in it was to increase the weight of the tools; but latterly the much greater depth of the wells has led to the employment of a combination of the rod system with a wire-cable system. The chief centre of the petroleum industry of Galicia is the prolific Tustanowice-Boryslaw field, which yields a very large proportion of the total output. Many of the wells here exceed 1000 metres in depth, and are costly to drill, but flowing wells are frequently obtained, and the production of these is so large that heavy expenditure in drilling is justified. The crude oil is of good quality, and yields all the usual commercial products, including paraffin wax.

The world's supplies of ozokerite are mainly obtained from the Boryslaw mines. The ozokerite deposit, which is unique in character, extends over a pear-shaped area, the richest part of which is only about 52 acres in extent, and is mined by means of shafts and drifts or galleries. It occurs in veins of varying thickness, and is mined by picks. The ozokerite is obtained partly in fragments of nearly pure material, but more largely in admixture with the matrix, from which it is separated by hand-picking or sorting and by the use of hot water, a further yield being obtained by the use of benzine as a solvent. The crude ozokerite, which is of dark greenish-brown colour, and about as hard as beeswax, is melted, cast into blocks, and delivered to the refineries, where it is treated with Nordhausen oil of vitriol and afterwards with charcoal. The purified and partly decolourised material, which is known as ceresin, has a m.p. of 61° to 78°, and is largely employed as an adulterant of, or even as a substitute for, beeswax in the manufacture of church candles. For the production of the substance of which ordinary candles of high melting-point are made, the crude ozokerite is subjected to distillation in a current of superheated steam, when about 60 p.c. of white wax of a m.p. of 140°F. is obtained. The by-products of the distillation consist of light oils and a semi-solid substance similar to vaseline, which, after purification, has been used by French perfumers as a substitute for lard in the process of *enfleurage*. The residue in the stills consists of a hard, black, waxy substance, which when incorporated with indiarubber and subjected to vulcanisation, yields the product termed *okonite*, used in coating electrical cables. Okonite is not only a good insulator, but is remarkably flexible and tough. From the residue a 'heel-ball,' employed to impart a black polished surface to the heels and soles of boots, and to the leather-work of harness, is also made (*v.* OZOKERITE).

Hungary. The oil-fields of Hungary geologically resemble those of Galicia, but the petroliferous area on the Hungarian side of the Carpathian range is comparatively narrow, and has not as yet assumed any great industrial importance.

Roumania.

As already stated, the petroliferous region of Roumania may be regarded as an extension of that of Galicia; it is also, doubtless, connected under the sea with that of the Caucasus. The Roumanian deposits may be traced by the outcrop from the Galician frontier to the Iron Gates, a distance of about 400 miles, and the width of the belt is from 15 to 20 miles.

The use of the 'liquid bitumen' of Roumania as a medicine, as an illuminating agent, and as a lubricant, was mentioned by the traveller Raicevich in 1750, but the existence of numerous pits and timbered hand-dug shafts of great age attests the fact that petroleum was systematically collected in the country long before that date. For many years after the introduction of drilling by steam-power in Galicia the petroleum of Roumania was still obtained in this primitive fashion, and the development of the industry was retarded, but similar methods are now adopted in both countries.

The expansion of the industry has been rapid, and bids fair to outstrip that of the corresponding industry in Galicia. The principal producing territories are in the districts of Prahova, Dimbovitza, Bacau, and Buzeu, and of these the first-named has hitherto been the most important.

The crude oil is of excellent quality, and in respect of the yield of the more volatile products occupies a position midway between those of Pennsylvania and Baku oils. The manufacture of fuel oil from the Roumanian crude petroleum is very largely carried on, although the residuum is also converted into lubricating oils to a considerable extent.

Sumatra, Borneo, and Java.[1]

Sumatra. The development of the oil-fields of Sumatra dates from 1885, when a flowing well was completed on a concession, granted two years previously, in Langkat, North Sumatra. In 1890 the Royal Dutch Company was formed to exploit another concession of oil-bearing lands in Langkat, and this company, besides drilling a number of wells during the ensuing five or six years, erected a refinery on the Bay of Aru, and laid a pipe-line to convey the crude oil from the wells to the refinery. The company also acquired and worked concessions in other districts, including Perlak, in the Atchin Residency, where highly productive spouting wells were drilled, and Palembang, South Sumatra. In 1897 the Sumatra Palembang Petroleum Company was formed, and this company in the course of the next few years obtained a large yield in the Palembang district of oil of low specific gravity (0·765 to 0·775), for the transport of which a pipe-line was laid to a refinery erected on the river Lalang. In the same year (1897) a third company, the Moeara Enim Company, was formed, to work concessions on the River Enim and elsewhere in Palembang and drilled a large number of wells, many of which were 'spouters' yielding from 400 to 800 tons daily of oil of sp.gr. 0·792. This company's refinery was built on the Musi, 3 miles below the town of Palembang, and the distillation of the crude oil was conducted on the continuous principle. In 1901 a fifth company, the Moesi Ilir Company, was added to the list, and commenced work on lands situated on the right bank of the Musi. The oil obtained here from spouting wells had a sp.gr. of 0·812 to 0·889. The company laid a pipe-line to Palembang, where a refinery was built. The prominent feature of the Sumatra petroleum is the large percentage of spirit yielded on distillation. This spirit has become a very important article of commerce, and its importation into Great Britain has been of the greatest service to the automobile industry, as the supplies of motor spirit would otherwise have been inadequate to meet the rapidly growing demand.

Borneo. The pioneers in petroleum development in Borneo were the Shell Transport and Trading Company, whose properties were transferred to the Nederlandsch-Indische Industrie en Handel Maatschappij. The territory over which the company acquired exploitation rights is situated on the southern half of the east coast of Borneo, and has an area of 500 or 600 square miles. It is bounded on the north-east by the Kutei or Mahakkam River, and it extends towards the south to Balik Papan Bay, but it embraces also a strip of land on the south of the bay. Drilling operations were commenced in December, 1896, but were not actively carried on until a year or two later. The company has drilled a large number of wells, of which the maximum depth is about 1500 feet, and many of these have been flowing wells yielding abundantly. The crude oil at first obtained at shallow depth was an asphalt-base petroleum of high specific gravity, but subsequently a lighter oil of the same character was obtained at greater depth, and still later a paraffin-base oil of high commercial value was found. The company's refinery is situated on the northern shore of Balik Papan Bay. The asphalt-base petroleum of Borneo gives a large yield of excellent fuel oil, and from the paraffin-base petroleum all the usual commercial products, including paraffin wax, are obtained.

Java. The petroleum industry of Java owes its inception to the enterprise of the brothers Stoop, whose interests were acquired by the Dordtsche Petroleum Maatschappij; since the year 1886 the industry has been rapidly progressive, and now occupies an important position. The chief producing territory is situated due south and south-west of the town of Surabaya, but there are also prolific deposits in the residency of Rembang. The depth of the wells range from 500 to 800 feet, and the drilling is chiefly done by the water-flush system. The average production of the wells is not large, but the yield is satisfactorily maintained. The crude oil has a sp.gr. of 0·825 to 0·916, and it yields a large proportion of solid hydrocarbons (paraffin) of unusually high melting-point.

British India.

Burma. At the end of the eighteenth century Major Symes described the petroleum wells 5 miles east of Yenangyaung, on the Irrawadi, as supplying 'the whole Empire and many parts of India with that useful product.' At that time the oil was obtained by the natives from comparatively shallow hand-dug wells, but since 1891 drilling operations have been actively conducted in this and other districts by the Burmah Oil Company, Ltd., a British organisation which was the pioneer in the present petroleum industry of Burma. The principal yield is obtained from the Khodoung field, immediately adjoining the areas on which the native wells were dug; but oil is also found at Singu and at Yenangyat, respectively about 25 miles nearer to, and 25 miles further from, Rangoon. The Khodoung (Yenangyaung) crude oil has a sp.gr. ranging from 0·737 to 0·899, and contains so large a proportion of solid hydrocarbons that it solidifies in cool weather. The Singu oil has a sp.gr. ranging from 0·731 to 0·904, and the Yenangyat oil ranging from 0·770 to 0·890. The wells are drilled by the American system. Formerly the crude oil was conveyed by bulk-barges on the Irrawadi to the refineries at Rangoon, but the Burmah Oil Company has recently completed a pipe-line 275 miles in length from the fields to the refineries. The company is under contract to supply the British Admiralty with oil fuel for the Navy, and has expended a large sum of money in making provision for this.

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[1] The Bataafsche Petroleum Maatschappij, of the Hague, now own or control all the petroleum production in the Dutch East Indies.

Assam. The Assam Oil Company, Ltd., has acquired the petroleum interests of the Assam Railways and Trading Company, Ltd., and the Assam Oil Syndicate, Ltd., and is continuing the work of development carried on by those companies in the Digboi field with uniformly successful results. The company has a refinery where all the usual commercial products, including paraffin wax, are manufactured.

Mexico.

The Mexican Eagle Oil Company, Ltd., own large areas of proved petroliferous lands, and three fields are at present being exploited at Tanguijo, Tierra Amarilla, and Potrero del Llano, in Northern Vera Cruz. Fuel oil from these fields is now being supplied to the Mexican Railway, the Tehuantepac National Railway, and various steamship companies, and the crude oil is also shipped to the company's refinery at Minatitlan. The company has recently acquired the oil interests of the firm of S. Pearson and Son, Ltd., who for some years have systematically explored the Isthmus region, where they have several hundred thousand acres of petroliferous lands. Several other companies are also taking part in the development of the Mexican petroleum industry.

An illustration of the difficulties and disappointments met with in the exploitation of oil lands is furnished by the following particulars of a well drilled at Dos Bocas in 1908. This well had reached a depth of 1824 feet, when a petroliferous formation charged with oil under immense pressure was suddenly and unexpectedly penetrated. In less than twenty minutes the ground round the well began to tremble and fissures appeared, some at a distance of as much as 250 feet from the well, from which oil and gas were discharged. One of these fissures extended under the boiler, and the gas was ignited. The well burned for 58 days, during which time the oil consumed was estimated to have amounted to 3,000,000 barrels. The flame reached a height of nearly 1500 feet, and at the broadest part had a diameter of nearly 500 feet. So bright was the light emitted that a newspaper was read by it at a distance of 11 miles. In addition to oil and gas, the well discharged immense quantities of water, at times at the estimated rate of 1,500,000 barrels a day, and with the liquid about 2,000,000 tons of solid matter was ejected, a crater being thus formed which ultimately had an area of 117,600 square metres. The fire was eventually extinguished by pumping sand into the crater with centrifugal pumps.

The output of petroleum in Mexico is rapidly increasing, and that country is now third in rank among the oil-producing countries of the world.

Japan.

The Japanese oil-fields extend from the western shore of Saghalin in the north, through the western part of the highlands of Hokkaido, and along the coast of the Sea of Japan, and thence, traversing the provinces of Mutsu, Ugo, Utzen, Echigo, and Shinano, reach to the coast of the Pacific Ocean in the province of Totomi in the south. There is also an oil-field in the northern part of the west coast of Formosa. The chief centre of the industry is in the province of Echigo, which produces about 99 p.c. of the total output of petroleum in Japan. The usual depth of the wells is from 600 to 1200 feet, and the American system of drilling is employed.

Germany.

Petroleum is found at Wietze, Steinförde, Oelheim, and elsewhere in the kingdom of Hanover; at Lobsann, Pechelbronn, Schwabweiler, and elsewhere in the neighbourhood of Hagenau, in Lower Elsass, including Altkirch, in Upper Elsass; and in the Tegernsee district in Bavaria. The crude oil of the Wietze-Steinförde district has a sp. gr. of 0·890 to 0·930. The sp.gr. of the Hagenau oil is 0·873, and that of the Tegernsee oil is 0·812.

Peru.

The petroliferous region of Peru extends about 250 miles in a northerly and southerly direction between the town of Tumbez, on the Gulf of Guayaguil, and Point Aguja, and about 150 miles east and west, from the Pacific coast to the slopes of the Andes. The northern fields, which are in the province of Tumbez, stretch from the Zarumilla River, which divides Peru from Ecuador, to the Mancora gully. The central fields comprise a part of the province of Paita, and extend from the Mancora gully to the south of the Silla de Paita and Foca point. The southern fields are situated in the province of Piura. The petroleum found in the hacienda La Mina Brea and Pariñas, which lies in the central portion of the petroliferous zone, was utilised by the Incas for centuries, and in the time of Pizarro it was collected in trenches and converted, by boiling it down, into a pitch of excellent quality, employed to line the porous earthen jars in which the Peruvians kept and transported their fermented liquors. In 1867, Mr. Prentice, a Pennsylvanian petroleum producer, commenced drilling wells in the Zorritos field, at the northern end of the belt, and subsequently disposed of the property to the Faustine G. Piaggio Petroleum Company. The crude oil has a sp. gr. of 0·810 to 0·840, and is rich in the more volatile hydrocarbons. In 1888 the hacienda La Mina Brea and Pariñas was acquired by Dr. Tweddle, and the London and Pacific Petroleum Company was formed. The area of the property is 600 square miles. The crude oil has a sp. gr. of 0·834 to 0·848, and yields as much as 18 p.c. of benzine. The Lobitos Oilfields, Ltd., is a British company, formed in 1908 to acquire the properties of the Peruvian Petroleum Syndicate, Ltd. The company's Lobitos property comprises an area of about 25 square miles on which a large number of productive wells have been drilled. The company also has drilling rights on a further 4560 acres in the Punta Restin oilfield, about 13 miles north of Lobitos.

Canada.

Canadian petroleum has been obtained hitherto only in the province of Ontario, although it occurs in other parts of the dominion. The petroliferous region of Ontario has an area of about 100 miles by 50 miles, but the developed territory is mainly confined to a belt 16 miles by 2 miles, situated about 16 miles east of Sarnia and extending nearly parallel with the St. Clair River. The sinking of wells in the Enniskillen district began in 1861, and the petroleum industry in Canada is, therefore, almost equal in age to that of the United States. Although many of the Canadian wells have yielded largely at first, their output has in most instances quickly diminished, and the production is mainly obtained from a large number of wells yielding only a few gallons each daily. Natural gas is also found in Ontario, and is utilised as a source of light and heat. The largest area over which petroleum indications occur in Canada lies in the region of the Athabasca and Mackenzie rivers, in the north-west part of the dominion, where immense deposits occur of so-called 'tar sands,' a fine-grained sandstone, saturated with inspissated petroleum. It has been estimated that the bituminous sands 'in sight' amount to 28·4 cubic miles, and that they contain 6·5 cubic miles, or 4,700,000,000 tons, of bitumen.

New Brunswick. The Maritime Oilfields Company, Ltd., are carrying out drilling operations under a concession, of an exceptionally favourable character, granted by royal charter in 1900, which gave the right to search for oil and gas over an area of 18,000 square miles and to select 10,000 square miles (more than one-third of the area of the province). The area selected is situated in the counties of Westmoreland, Albert, King's, Queen's, Sunbury, Kent, Northumberland, Gloucester, Restigouche, and a portion of York, and is traversed by several anticlinals, on one of which, in Westmoreland county, wells have been drilled successfully, a large yield of natural gas, in addition to oil, having been obtained. The crude petroleum is of excellent quality, with a paraffin base, and yields, in addition to 34 p.c. of kerosene, a fuel oil of high calorific value, containing only 0·14 p.c. of sulphur.

Italy.

The collection of the petroleum of Miano di Medesano was the subject of a concession granted by the Ducal Chamber in 1400, and the celebrated petroleum of Modena, at one time largely used for medicinal purposes, for lighting, and in the preparation of varnishes and paints, was discovered in 1640 by Ariosto. The petroleum of Montechino was apparently not known prior to the commencement of the eighteenth century, whilst the deposits of Ozzano and Rico di Fornovo did not attract attention until early in the nineteenth century, and those of Neviano de' Rossi, Salsomaggiore, and Lesignano de' Bagni were found still later. Petroleum from the wells of Amiano, on the Taro, was used for lighting the cities of Genoa, Parma, and Borgo San Donnino as early as 1802. The districts in Italy in which petroleum is found in commercial quantities are (1) the zone of Emilia; (2) the valley of the Pescara, in the province of Chieti; and (3) the valley of the Liri, near San Giovanni Incarico, about midway between Rome and Naples. The zone of Emilia occupies the southern parts of the provinces of Piacenza, Parma, Modena, and Bologna. Some of the Italian crude petroleum has a specific gravity as low as 0·805, and is of amber colour, but unfortunately the quantity hitherto obtained has been small.

Other sources of supply.

In addition to the sources specified in the tabular statement of production, and some others incidentally described in the preceding account, there are several potentially important petroleum-producing countries to which reference should be made.

Persia.

The occurrence of petroleum in Persia has been mentioned by travellers from very early times, and its collection from the pits of Kir ab ur Susiana (Kirab), 57 miles north-west of Shuster, was fully described by Herodotus. The petroleum deposits extend in a general south-easterly direction, from the Turco-Persian frontier, about 100 miles north of Bagdad, to the Persian Gulf. In the course of surveys conducted a few years ago, specially favourable indications were found in two districts, one at Zohab, in lat. 34° 18′ N., long. 45° 55′ E., and the other near Shuster and Ahwaz, on the Karun River, at the head of the Persian Gulf. In 1903–4 two wells were drilled at Tchiah Sourkh, near Kasr-i-Shirin, in the Zohab district, by Mr. W. K. D'Arcy, under a unique concession granted by the Shah, giving petroleum rights over the whole Persian Empire, with the exception of certain provinces on the Caspian Sea. One of these wells began flowing at a depth of 800 feet, and the other, at a greater distance from the crest of the anticlinal, reached oil at 2100 feet. The crude petroleum had a sp. gr. of 0·815, and was of exceptionally high quality. Subsequently the Burmah Oil Company, Ltd., became associated with Dr. D'Arcy in the conduct of the development, and drilled several highly productive wells in the second of the two districts referred to. In 1909 the Anglo-Persian Oil Company, Ltd., was formed to take over the concession, and has actively continued the work. The company is constructing a refinery and laying a pipe-line. It may here be mentioned that the Persian petroleum deposits extend into Turkey, and that very promising indications are met with in Mesopotamia.

Egypt.

The oil deposits of the Red Sea have been known from time immemorial, but attention was specially directed to them during the latter part of the last century by the successful results of the exploratory work carried out by de Bay at Jebel-Zeit, about 160 miles from Suez, and Jemsah, 13 miles south of Jebel-Zeit. In 1905 the Egyptian Petroleum Company, Ltd., acquired a concession over a large area at Jemsah. In 1907 the Egyptian Oil Trust, Ltd., took over the concession, and drilled a number of highly productive wells. On a portion of the area the work has been continued by the Red Sea Oilfields, Ltd., which was formed in 1910. The Anglo-Egyptian Oilfields, Ltd., the management of which is vested in the Anglo-Saxon Petroleum Company, Ltd., has recently acquired the licenses and assets of the Egyptian Oil Trust, Ltd., with a view to the active development of the field, and shipments of the crude oil have already been made. Drilling operations are also being conducted by the Sinai Petroleum Syndicate, Ltd., on the Sinai Peninsula.

Trinidad.

The 'Pitch Lake' of Trinidad, which is the most important, if not the largest, deposit of solid or semi-solid bitumen, was visited in 1595 by Sir Walter Raleigh, who reported that he saw there 'that abundance of stone pitch that all the ships in the world might be laden from thence.' The area of the deposit is about 100 acres, and on the basis of an average depth of 20 feet, the quantity of the material obtainable has been estimated at over 3,000,000 tons. Gesner states, in his Treatise on Coal, Petroleum, &c. (New York, 1861), that it was from Trinidad asphalt that he first prepared kerosene.

Petroleum apparently occurs over a great part of the southern half of the island. The first important concession of oil-bearing territory was granted some years ago, on the initiative of Mr. Randolph Rust. It embraces an area of more than 50 square miles at Guayaguayare in the south-eastern corner of the island. Although the early drilling operations were attended with success, very little progress was made in the work of development until the concession passed into the hands of the General Petroleum Properties of Trinidad, Ltd. Among a large number of other companies recently formed to participate in the exploration and exploitation of the oil lands of Trinidad, one of the most important is Trinidad Oilfields, Ltd., which acquired the rights over areas in the Guapo and La Brea districts on which successful results had already been obtained by the Trinidad Petroleum Company, Ltd. It is, however, in the neighbourhood of the Pitch Lake that the greatest progress has been made. Here, through the enterprise of the American concessionaires of the lake and their associates, a number of prolific wells have been drilled, a refinery has been built, and the first shipment of the oil was made in the spring of 1911. There are grounds for hope that Trinidad may become an important source of oil fuel for the British Navy.

Barbados.

The crude petroleum of Barbados, under the name of 'Barbados tar,' was formerly an article of commerce, and occupied an important place as a medicinal agent. It was obtained from a group of hand-dug shafts known as the Lloyd wells, in the Scotland district of the island. Drilling has been conducted in this district by the West Indian Oil Syndicate, Ltd., and subsequently by the West Indian Petroleum Company, Ltd., but only small quantities of oil have been met with.

Venezuela.

The petroleum deposits of Venezuela resemble those of Trinidad, and will probably become of great commercial importance. There are many highly promising petroliferous areas of great extent, and in the State of Bermudez there is a deposit of asphalt far larger than the Pitch Lake of Trinidad.

Colombia.

Remarkable indications of the presence of petroleum are reported to occur in Colombia. As many as 40 petroleum springs have been found at a distance of 1 to 3 miles from the Gulf of Uraba, near the Arboletes, one of which is said to yield enough oil to fill a six-inch pipe. Other springs occur on the plain of Medina, about 9 miles from the River Upia, a tributary of the Meta.

Ecuador.

The existence of petroleum in the Santa Elena district, about 64 miles west by south of the port of Guayaquil, has been known for more than two centuries, and the oil has from very early times been collected in a primitive fashion for local use.

Argentina.

On the eastern slopes of the Sierras of the Andes, and elsewhere, there are promising indications of the occurrence of petroleum; but although in some localities oil has been found in quantity, drilling operations have not been generally successful.

Newfoundland.

The existence of petroleum on the west coast of Newfoundland has been known for about a century, for it was in 1812 that Mr. Parsons, after whom Parsons' Pond is named, used the crude oil of this district as a cure for rheumatism. Drilling operations are now being conducted at Parsons' Pond.

Alaska.

Several wells have been drilled in the neighbourhood of Katalla and excellent results obtained, in respect alike of the abundance of yield and of the quality of the oil. The producing territory has been acquired by the Amalgamated Development Company, an organisation in which Canadian capitalists are largely interested.

New Zealand.

The principal indications occur (1) in the Taranaki district on the west coast of the island at New Plymouth and on the adjacent

Sugar Loaves Islands; (2) on the east coast along a belt of country extending from Horoera Point, near the East Cape, to the Okahuatin Block, 30 miles west of Gisborne (Poverty Bay); and (3) at Kotuku, near Lake Brunner, South Island. Wells drilled at New Plymouth have yielded petroleum of excellent quality, with a sp.gr. of 0·840, and containing a large proportion of solid hydrocarbons. The exploratory drilling carried out many years previously in the Poverty Bay district was not attended with success, but as the result of further recent study of the geological conditions, it is hoped that both here and in the Taranaki district a large output may eventually be obtained.

THE TESTING OF CRUDE PETROLEUM AND OF PETROLEUM PRODUCTS.

1. *Crude petroleum.*

The examination of crude petroleum which the chemist is called upon to conduct in the laboratory for commercial purposes usually includes the estimation of water and sediment, the ascertaining of the specific gravity, flashing-point, setting-point, and viscosity, and the determination of the percentage and character of the products yielded on fractional distillation. The test recommended by Engler gives most useful information in regard to the commercial value of a sample of crude petroleum. It consists in carefully distilling the oil in a Wurtz flask, and noting the percentages of distillate obtained below 150° F. and either 300° F. if the hydrocarbons present are mainly those of the methane series, or 285° F. if they are principally naphthenes, the first fraction consisting of benzine and the second of kerosene.

The natural lubricating oils (crude petroleums) of Pennsylvania, Ohio, West Virginia, and Kentucky have been classified by the West Virginia Transportation Company according to specific gravity, and subjected to the following test:—

'In receiving and making delivery of oils shipped by the company, the water and sediment contained therein shall be determined by mixing an average sample with an equal quantity of benzine,[1] and subjecting the mixture to 120°F. in a graduated glass vessel for not less than six hours, after which the mixture cools and settles not less than two hours for light grades, three hours for A grade, four hours for B grade, six hours for C grade, eight hours for D grade, and eighteen hours for heavier grades.' The grades are as follows:—

A. 37·1° Baumé (about 0·838 sp.gr.) and lighter.

B. 33° to 37°B. (0·859 to 0·838 sp.gr.).
C. 31·6° to 32·9°B. (0·870 to 0·859 sp.gr.).
D. 30·6° to 31·5°B. (0·873 to 0·872 sp.gr.).
E. 29·6° to 30·5°B. (0·877 to 0·873 sp.gr.).
F. 28·6° to 29·5°B. (0·883 to 0·877 sp.gr.).
G. 28·5°B. (0·883 sp.gr.) and heavier.

Ordinary crude petroleum, from which kerosene and the other usual commercial products are manufactured, is in the United States required to conform to the following rule of the New York Produce Exchange, except in regard to specific gravity, as to which the restriction has been relaxed, in consequence of the fact that much of the crude petroleum now obtained has a specific gravity Baumé below 43°:—

'Crude petroleum shall be understood to be *pure natural oil*, neither steamed nor treated, free from water, sediment, or any other adulteration, of the gravity of 43° to 48°B. (0·809 to 0·786 sp.gr.).'

In order to determine whether the petroleum is a 'pure natural oil' a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the specific gravity of the several distillates is determined. The following results obtained in the examination of two typical samples indicate the form of the certificate handed to the buyer:

Oil from Parker District. Gravity 46° *Baumé.*

1st Product	. 72°B.	6th Product	. 46°B.
2nd "	. 62°B.	7th "	. 42°B.
3rd "	. 57°B.	8th "	. 41°B.
4th "	. 53°B.	9th "	. 42°B.
5th "	. 49°B.		

Oil from Bradford District. Gravity 43° *Baumé.*

1st Product	. 71°B.	6th Product	. 41°B.
2nd "	. 60°B.	7th "	. 40°B.
3rd "	. 54°B.	8th "	. 41°B.
4th "	. 49°B.	9th "	. 42°B.
5th "	. 45°B.		

The regular gradation in the specific gravities of the fractions exhibited in the foregoing certificates is taken to be a satisfactory indication that the oil is a natural product.

The examination of a sample of crude petroleum with the object of ascertaining the percentage of commercial products obtainable is not always an easy operation, especially when the quantity available is small. The writer is accustomed to conduct the fractional distillation in a glass retort embedded in sand, and to compare the results obtained with those furnished by samples of crude petroleum the yield of products from which on the commercial scale is known, but even in these circumstances some experience is needed in certain cases. The difficulties encountered arise from the circumstances that in practice in the United States some of the intermediate hydrocarbons are 'cracked,' and thus converted into kerosene to a larger extent than usually occurs when the distillation is conducted in a small retort in the laboratory, and that, on the other hand, the heavy hydrocarbons composing the lubricating oil are less 'cracked' when properly distilled with the aid of steam on the large scale than when distilled on the small scale. The determination of the percentage of solid hydrocarbons is also attended with considerable difficulties when the quantity of material operated upon is small. In every case the aim should be to reproduce as far as possible the conditions of practical working.

2. *Petroleum spirit.*

In the testing of petroleum spirit, including petrol, gasoline, benzine, &c., it is usual to determine the specific gravity and range of boiling-points, and it is generally desirable to make a fractional distillation of the sample in order to ascertain the percentage boiling below a series of temperatures increasing by regular intervals. 100 c.c. should be distilled from a Wurtz flask which is supported on a sand dish and has the following dimensions :—

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[1] In the case of the more viscous descriptions of petroleum, the writer finds that further dilution is desirable. The benzine used should be previously saturated with water.

Bulb 2¾ ins. in diameter; neck ¾ ins. in diameter, 5¾ ins. long; exit tube 2½ ins. above shoulder. The tube of the Liebig condenser employed is 24 ins. long. The thermometer having been adjusted with its bulb at first just immersed in the liquid, is gradually raised, as soon as ebullition becomes active, so that its bulb is slightly below the rising level of the vapour (which can be seen with a strong illumination). The temperature at which the first drop falls from the end of the exit tube of the flask is taken as the initial boiling-point of the sample. The percentages collected in a 100 c.c. measure glass at different thermometer-readings are recorded, together with the final boiling-point, or temperature at which the flask becomes dry. Deodorised American petroleum spirit should have no disagreeable odour either in bulk or when evaporated on the hand. A small quantity evaporated in a basin over the water-bath should leave no oily residue. When petroleum spirit is used as a turpentine-substitute in paints it is important that it should contain no sulphur compounds. For the detection of these the sample may be boiled for a few minutes with alcohol and a few drops of ammonia, and nitrate of silver solution then added, when there should be no brown colouration.

The presence of sulphuric acid may be detected by agitating the spirit with warm water, separating the water (which should exhibit no acid reaction), and adding to it a few drops of barium chloride solution.

3. *Kerosene.*

For ordinary commercial purposes the only characteristics which are noted in the examination of kerosene are the colour, the odour, the specific gravity, and the flashing point or fire-test. In certain cases, however, special tests are applied with the object of ascertaining whether the oil is of satisfactory burning quality, is of natural composition, has been properly treated with acid, has been sufficiently washed, and is free from sulphuric acid, sulphonates, and sulphur in other forms.

(*a*) *Colour.*—Formerly it was the practice to estimate the colour of a sample by comparing it with that of a standard sample, the two oils being placed in bottles of the same size. Such a method did not, however, admit of an accurate comparison being made, and in the year 1870 the writer adopted the plan of placing the samples in long glass cylinders which were held in a frame in such manner that the images of the glass bottoms of the cylinders could be viewed side by side in a mirror. This arrangement was found to present marked advantages in the case of a fluorescent liquid like petroleum, but the system was open to the objection that the standard samples were very liable to become altered in colour, and required to be frequently verified and corrected by experts. Moreover, the adoption by the Petroleum Association of London of precise conditions of contract necessitated the provision of a more accurate and unerring test of colour. Accordingly, the Committee of the Petroleum Association decided, under the advice of the writer, to employ an instrument devised by Mr. R. P. Wilson for use with stained glass standards. This apparatus (Fig 2), which has admirably fulfilled the object in view, consists of two similar tubes, closed at each end by a screw cap carrying a disc of stout glass. These tubes are placed on a stand at a convenient angle above a small mirror, by means of which light is reflected upwards through them. At the upper ends of the tubes is a box containing two pairs of prisms so arranged that the light passing from the mirror is twice reflected, and is thus brought into an eye-piece surmounting the box. One of the tubes is completely filled with the sample of oil to be tested, the length of the column of liquid being sixteen inches, and beneath the other tube, which remains empty, a disc of stained glass is placed. On applying the eye to the eye-piece the circular field is seen to be divided through the centre by a sharp line formed by the junction of the prisms, the two halves being tinted to an extent corresponding with the colour of the oil and that of the standard glass respectively. The glass standards representing the various grades of colour recognised in the trade are prepared by the Tintometer, Ltd., of Salisbury. They are five in number, and are thus designated :

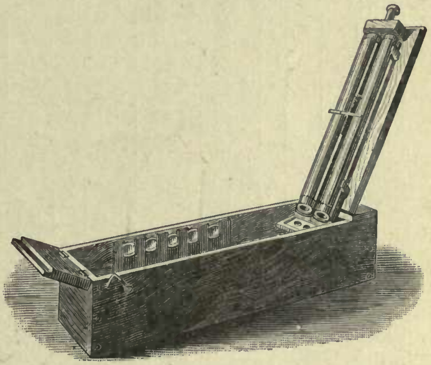

FIG. 2.

1. Water white.
2. Superfine white.
3. Prime white.
4. Standard white.
5. Good merchantable.

The Wilson chromometer admits of an accurate comparison being made, but where the colour of the sample lies between those of two standards, there is an absence of precision in the statement of the result of the test. This is not attended with any practical inconvenience where the instrument is simply used for ordinary routine work, but the writer has frequently found it necessary to record the precise colour of a sample, or to state by how much that colour falls short of a stipulated grade. To meet this want a modification of the chromometer already described was designed by Stammer. In this apparatus there is a provision for shortening the length of the column of oil, so that, starting with a standard of somewhat paler tint than the oil, the colour of the oil may be registered in terms of the standard. Messrs. Schmidt and Haensch, the well-known philosophical instrument makers of Berlin, have devoted a good deal of attention to the improvement of Stammer's original instrument, and have devised a colorimeter which the writer has used, and of which he has formed a favourable opinion. In the construction of this apparatus (Fig. 3) Messrs. Schmidt and Haensch have desired to provide for the use of only one glass standard, so that all recorded determinations of colour may be strictly comparable. This would be a distinct advantage, since the relation between the various standards enumerated is a purely arbitrary one; but unfortunately the range of colour is necessarily so wide that if a standard suitable for water-white oil is employed, the column needs to be so much decreased in length for oils of comparatively dark colour that the sensitiveness of the instrument is seriously impaired. To overcome this defect, Mr. Robert Redwood has made several important alterations in the instrument, which, while largely increasing its sensitiveness, admit of the colour of any sample of kerosene being precisely recorded on a scale ranging from water white (1) to good merchantable (5), the space between any two of the colours being divided into ten equal parts, so that the colour of a sample midway between water white and superfine white would be expressed as 1·5. This instrument has been in use in the writer's laboratory for many years, and has given very satisfactory results.

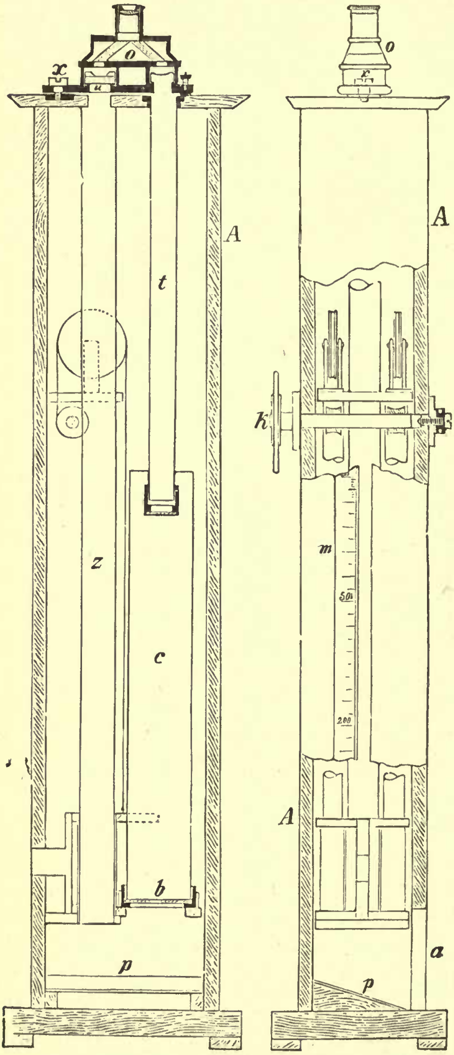

FIG. 3.

A. Case. *a*. Opening for passage of light to reflector. *b*, *c*. Cylinder, with glass bottom, for oil under examination. *k*. Hand-wheel for raising or lowering cylinder *b*, *c*. *m*. Graduated scale showing length of column of oil through which light is passing. *o*. Optical arrangement (prisms and eye-piece). *p*. Reflector to project light upwards through the parallel tubes and the prisms into the eye-piece. *t*. Tube closed at the bottom by a glass plate. *u*. Coloured glass disc. *x*. Screw on which the optical arrangement may be turned to insert or remove the disc *u*. *z*. Tube open at both ends.

(*b*) *Odour.*—The determination of odour requires considerable experience, as it is necessarily a matter of judgment, and due consideration has to be given to the origin and grade of the oil. It is usual to certify that the odour is good merchantable, or not good merchantable, as the case may be.

(*c*) *Specific gravity.*—This is ordinarily determined by the use of a hydrometer, but the Westphal or the Sartorius specific gravity balance will often be found a preferable instrument. In the case of oil imported in bulk, where the weight of the oil is calculated from the volume at a given temperature, the specific gravity should be accurately determined by the use of the specific gravity bottle.

(*d*) *Flashing-point and fire-test.*—This is, at any rate from one point of view, by far the most important test to which kerosene is subjected, since the petroleum trade is in most parts of the world conducted under legal restrictions in regard to the temperature at which the oil either commences to evolve inflammable vapour or takes fire and continues to burn. The manufacturer of kerosene has on the one hand to avoid introducing into or leaving in the oil such of the more volatile hydrocarbons as would either actually or in the opinion of the Legislature render the fluid unsafe for use in lamps of the ordinary construction, and on the other hand to arrest the collection of the kerosene distillate before the process of distillation has resulted in the addition to the product of the denser hydrocarbons in such quantity as to impair the burning quality. The limitation of the specific gravity was found to be an effectual means of preventing the introduction into the oil of an undue proportion of the heavier hydrocarbons, but afforded no check upon the inflammability of the oil; accordingly, in the early days of the petroleum industry, it was customary in the United States to test the oil by pouring it upon warm water and applying a lighted taper to the surface, or by warming the oil in a cup placed in hot water, and applying a flame, the temperature at which the oil gave off ignitable vapour being termed the 'flashing-point,' and that at which it took fire the 'fire-test.' When, however, it became recognised that legal restrictions in regard to the inflammability of kerosene were necessary in the interests of public safety, special forms of apparatus for the testing of flashing-point and igniting-point were devised. The earliest of these testing instruments, known as

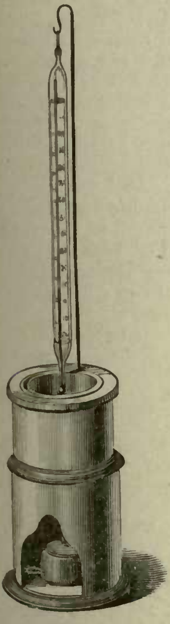

FIG. 4.

Tagliabue's open-cup tester (Fig. 4), was constructed by an instrument-maker of that name in New York. It consists simply of a glass cup to hold the oil, placed in a small copper water-bath, heated by a spirit lamp. A thermometer is suspended in the oil, and the temperature is noted at which, on passing a lighted splinter of wood across the surface of the oil, there is either a flash of ignited vapour, or on a further increase of temperature the oil ignites and continues to burn. The English Petroleum Act, passed on July 29, 1862, provided that 'Petroleum for the purposes of this Act shall include any product thereof that gives off an inflammable vapour at less than 100° of Fahrenheit's thermometer.' The method of testing was, however, not defined, and the Act was practically inoperative. Accordingly, on July 13, 1868, an amending Act was passed, which prescribed the form of apparatus and method of testing to be adopted, and defined 'petroleum' for the purposes of the two Acts as including 'all such rock oil, Rangoon oil, Burmah oil, any product of them, and any oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any product of them, as gives off an inflammable vapour at a temperature of less than 100° of Fahrenheit's thermometer.' The prescribed apparatus for testing consists of a slightly conical oil cup of thin sheet-iron, provided with a flat rim, and a raised edge ¼ in. high. Across the cup and fixed to or resting on the edge is a wire, which is thus ¼ in. above the flat rim. The oil-cup is supported by the rim in a tin water-bath. The outer vessel having been filled with 'cold or nearly cold water,' as much of the oil to be tested is poured into the cup as will fill it without flowing over the flat rim, and a thermometer with a round bulb, and so graduated that every 10°F. occupies not less than ½ in. on the scale, is then suspended in the oil so that the bulb is immersed about 1½ in. beneath the surface. A screen of pasteboard or wood of specified dimensions having been placed round the apparatus, a 'small' flame is applied to the bottom of the water-bath, and when the temperature of the oil has reached 90°F., a 'very small' flame is passed across the surface of the oil on a level with the wire, this application of the test-flame being repeated for every rise of 'two or three' degrees in temperature, until a 'pale-blue flicker or flash' is produced. The temperature at which this occurs having been noted, the experiment is repeated with a fresh sample of the oil, withdrawing the source of heat when the temperature approaches that noted in the first experiment, and applying the test-flame at every rise of two degrees.

The greater part of the earlier petroleum legislation in the United States was based upon fire-test and not upon flashing-point, but in several of the States the petroleum laws now prescribe a test of flashing-point. In 1879 the New York Produce Exchange adopted the Saybolt Electric Tester (Fig. 5), which is an open-cup instrument wherein the ignition is effected by means of an electric spark from a small induction coil, the spark being caused to pass when required between platinum points at a fixed distance above the surface of the oil. The official directions for the use of the apparatus are as follows:—

'Fill the metal bath with water, leaving room for displacement by the glass cup. Heat the water until the bath thermometer indicates 100°F., at which point remove the lamp. Fill the glass cup with oil to top line, indicated by the rim surrounding cup, which is one-eighth of an inch below top edge of the cup. See that there is no oil on the outside of the cup, nor upon the upper level edge, using paper to clean cup in preference to cotton or woollen material. See that the surface of the oil is free from air bubbles before first flash is produced. Lift the cup steadily with left hand and place in the bath. Suspend the thermometer with the bulb of same immersed just from view under the surface of oil. Adjust the flashing bar and immerse the battery zincs in fluid. Try for first flash every degree until the same is obtained. Attain flash by producing spark with one stroke of the key. The stroke on the key should be such as in telegraphy is used to produce what is called a dot, that is a short quick stroke. The first flash produced from 110° test oil is generally obtained when the temperature of the oil has arrived at 90°. The temperature of the bath at 100° (as per note above) will carry the oil to about 90°, or, in other words, to about the first flashing-point, without the aid of a lamp. When the thermometer in the oil indicates 90°, introduce lamp under the bath, and do not remove until the operation is finished. The temperature of oil when placed in bath should not be lower than 55° nor higher than 70°F. The flashing bar must be free from oil before adjusting for test. Draughts of air must be excluded from the apartment wherein tests are made.

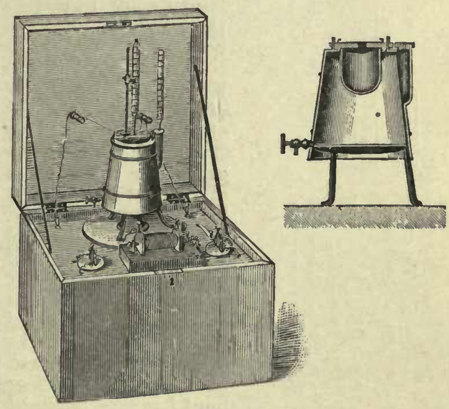

FIG. 5.

Oil of 110° and upwards shall (after first flash) be flashed at 95, 100, 104, 108, 110, 112, 115. Oil of 120° and upwards, after first flash, 100, 105, 110, 115, 118, 120, 122, 125. Oil of 130° and upwards, every five degrees after first flash, until burning-point.'

Prior to the introduction of the Saybolt Tester, Arnaboldi constructed an open-cup tester similar to Tagliabue's, but of greater capacity, and provided with a mechanical arrangement for passing the test-flame over the oil.

The directions for applying the test given in the English Petroleum Act of 1868 were found to be insufficiently precise, and much difference of opinion existed as to the interpretation of the words 'small flame' and 'very small flame,' with the result that dealers were proceeded against, and in some cases convicted of selling kerosene declared by the local authorities to have a flashing-point below the legal limit of 100°F., but which had been tested by independent experts with satisfactory results. Moreover, the open-cup system of testing was found by experience to be incapable of furnishing trustworthy results in the hands of unskilled persons.

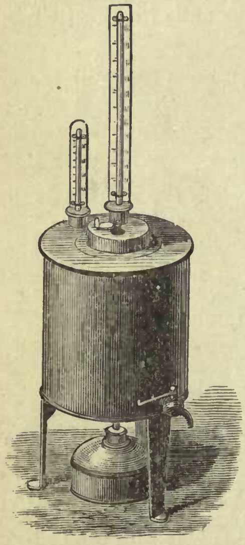

FIG. 6.

Accordingly, Mr. Keates, in his capacity of consulting chemist of the Metropolitan Board of Works, suggested the substitution of a closed cup (Fig. 6) for the open one, and in 1871 a Bill to legalise this alteration, as well as to amend the law in several other respects, was introduced into Parliament. In consequence, however, of the test standard or limit having been fixed by Mr. Keates at a point (85°) which it was contended was considerably higher than the equivalent of the existing standard, the Bill was opposed by the petroleum trade, and the proposal to change the form of apparatus was withdrawn; the Bill, which passed through the final stage on August 11 in that year, repealing the two previous Acts, but again prescribing the use of the open test specified in the Act of 1868. In the following year the subject of petroleum testing was inquired into by a Select Committee of the House of Lords, and a great deal of conflicting evidence was taken, but no satisfactory conclusion was arrived at. Therefore, in July 1875, with the concurrence and approval of the Metropolitan Board of Works and of the Petroleum Association, Sir Frederick Abel was requested by the Government to undertake an investigation with the object of placing the subject of petroleum testing upon a satisfactory basis. The formulated questions submitted to Sir Frederick Abel were the following:

'1. Whether the method of testing petroleum as prescribed in Schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is such as uniformly to ensure reliable and satisfactory results.

'2. If not, what alterations in the method of testing petroleum should be adopted to secure such results, due regard being had to the fact that the testing must, in many instances, be carried out by persons who have had comparatively little experience in conducting delicate experiments.

'3. Assuming it to be, in your opinion, desirable to obtain a "flashing-test" for petroleum, whether the present "flashing-point" of 100°F. (or its equivalent under any modified method of testing which you may propose) is, in your judgment, calculated to afford adequate protection to the public, without unduly interfering with or restricting the trade; if not, what alteration in this respect should be made.'

After a prolonged and exhaustive experimental inquiry, in which Dr. Kellner rendered valuable assistance, Sir Frederick Abel presented to the Secretary of State an elaborate report, dated August 12, 1876, wherein the questions enumerated were thus answered:

(1) The method of testing petroleum as prescribed in schedule 1 of the Petroleum Act, 1871 (34 & 35 Vict. c. 105), is not 'of a nature uniformly to ensure reliable and satisfactory results.'

(2) A method of testing petroleum has been elaborated for adoption in place of that prescribed by the Petroleum Act, 1871, due regard having been had to the fact 'that the testing must in many instances be carried out by persons who have had comparatively little experience in conducting delicate experiments.' This method, while resembling in its general nature the one hitherto used, is free from the defects inherent in the latter, and is so arranged that it can be carried out, with the certainty of furnishing uniform and precise results, by persons possessing no special knowledge or skill in manipulation. With ordinary attention in the first instance to simple instructions, different operators cannot fail to obtain concordant results with it, and it is so nearly automatic in its nature that it is not, like the present method of testing, susceptible of manipulation so as to furnish different results at the will of the operator.

(3) There are not, in my judgment, any well-established grounds for considering that the present flashing-point of 100°F. is not 'calculated to afford adequate protection to the public.'

(4) With the employment of the new test, a minimum flashing-point should therefore be adopted, which is equivalent, or as nearly as possible so, to the flashing-point of 100°F., as furnished by the present test.

It will be obvious that the determination of the equivalent test standard was not an easy part of Sir Frederick Abel's task, since the Abel tester furnishes no exception to the rule that the flashing-point of a given example of petroleum is far lower in a closed than in an open vessel, and it was therefore necessary to deal with the conflicting views already referred to as to the proper mode of conducting the test with the open-cup instrument in order to determine the equivalent standard. The writer assisted Sir Frederick Abel in the conduct of this portion of the inquiry, but before the test standard was even provisionally fixed, Mr. T. W. Keates, as representing the Metropolitan Board of Works, and Mr. John Calderwood, on behalf of the Scottish Mineral Oil Association, were also consulted. Eventually, as the result of the joint experiments, it was decided that the difference between the flashing-points obtained with the open-cup instrument and the Abel tester ranged from 25° to 29°F. Adopting the mean difference of 27°, the new standard was accordingly fixed at 73°F.

After the presentation of the report, the writer proceeded to apply the two tests to 1,000 representative samples of kerosene, with the result that the figures provisionally adopted were confirmed.

The ultimate outcome of Sir Frederick Abel's painstaking investigation was the legalisation by Parliament, on August 11, 1879, of what is now so well known as the Abel Test. The instrument and its use are thus described in the Petroleum Act :—

First Schedule.—Mode of testing petroleum so as to ascertain the temperature at which it will give off inflammable vapour.

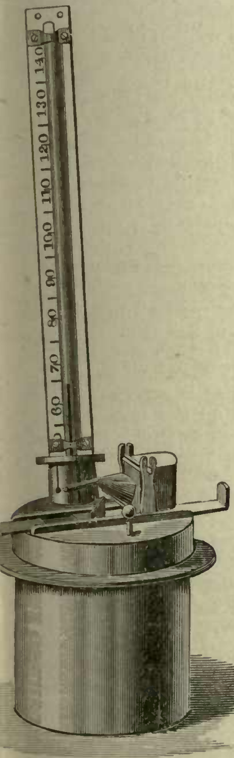

Fig. 7.

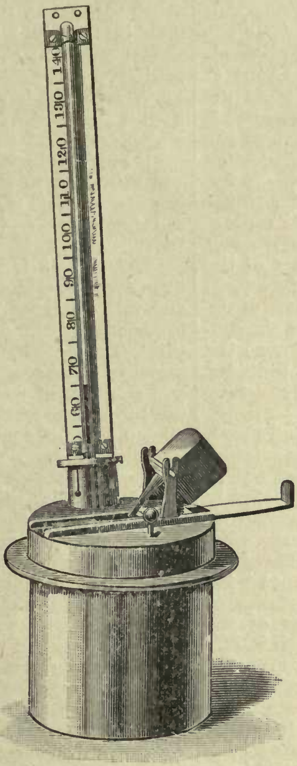

Fig. 8.

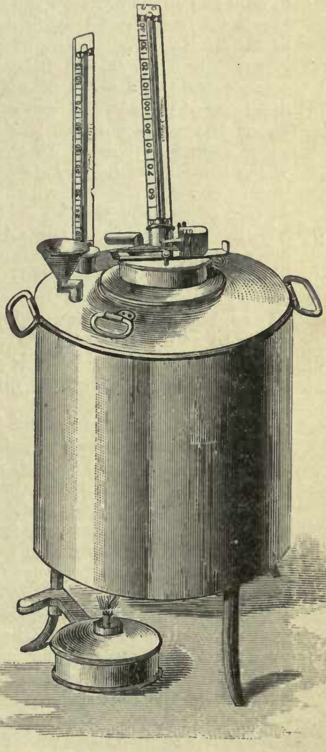

Fig. 9.

Specification of the test apparatus

(Figs. 7, 8 and 9).

The following is a description of the details of the apparatus :—

The oil cup (Fig. 7) consists of a cylindrical vessel 2″ diameter, 2$\frac{2}{10}$″ height (internal), with outward projecting rim $\frac{5}{10}$″ wide, $\frac{3}{8}$″ from the top, and 1$\frac{7}{8}$″ from the bottom of the cup. It is made of gun-metal or brass (17 B.W.G.) tinned inside. A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is 1$\frac{1}{2}$″. The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of trunnions, upon which it may be made to oscillate ; it is provided with a spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer, when inserted to its full depth, shall be 1$\frac{1}{2}$″ below the centre of the lid.

The cover is provided with three square holes—one in the centre, $\frac{5}{10}$″ by $\frac{4}{10}$″, and two smaller ones, $\frac{3}{10}$″ by $\frac{2}{10}$″, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid (Fig. 8). Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test-flame to be used.

The bath or heating vessel (Fig. 9) consists of two flat-bottomed copper cylinders (24 B.W.G.) —an inner one of 3″ diameter and 2½″ height, and an outer one of 5½″ diameter and 5¾″ height; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to inclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about ⅜″; that is, its diameter is about $\frac{6}{8}$″ greater than the body of the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil lamp is one-half of an inch. A split socket similar to that on the cover of the oil cup, but set at a right angle, allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is 6½″. One of the three legs of the stand serves as a support for the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is 1″.

Two thermometers are provided with the apparatus—the one for ascertaining the temperature of the bath, the other for determining the flashing-point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about 90° to 190° Fahrenheit. The scale (in degrees of Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about 3½″, measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about 55°F. to 150°F.; it measures from end of ivory back to bulb 2¼″.

Note.—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade.

Directions for applying the flashing-test.

1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

2. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130°F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

When a test has been completed, this water-bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 of an inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil-lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65° the samples to be tested should be cooled down (to about 60°) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5 The test-lamp is then placed in position upon the lid of the cup, the lead line or pendulum,[1] which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to

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[1] The pendulum is 24 inches in length from the point of suspension to the centre of gravity of the weight. The writer has found it convenient to employ a synchronised metronome.

be commenced, the test flame being applied once for every rise of one degree in the following manner:—

The slide is slowly drawn open while the pendulum performs three oscillations and is closed during the fourth oscillation.

Note.—If it is desired to employ the test apparatus to determine the flashing-point of oils of very low volatility, the mode of proceeding is to be modified as follows:—

The air-chamber which surrounds the cup is filled with cold water to a depth of 1½ inches, and the heating-vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120°F. instead of with cold water.[1]

In order to deal with the difficulty arising from the sluggish flow of the convection currents, and the consequent low reading of the thermometer, when viscous samples are tested, and, in addition, to make provision for the testing of solid petroleum mixtures, an Order in Council (Statutory Rules and Orders, 1907, No. 483) was issued on May 7, 1907, the Schedule of which is as follows:—

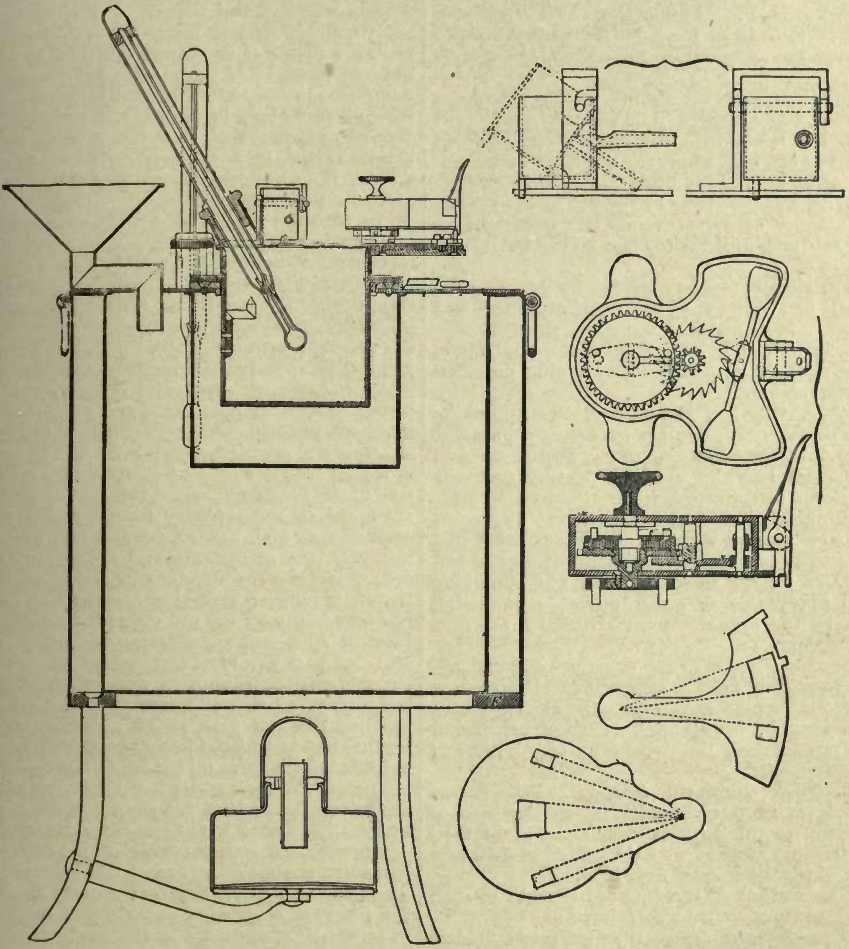

Fig. 10.

Schedule.—Directions for Testing Petroleum Mixtures.

1. *Liquid Mixtures.* Where the petroleum mixture is wholly liquid, flows quite freely, and does not contain any sediment or thickening ingredient, such mixture shall be tested in the manner set forth in Schedule One to the Petroleum Act, 1879.

2. *Viscous and Sedimentary Mixtures.* Where the petroleum mixture contains an undissolved sediment, as in the case of some metal polishes, which can be separated by filtration or by settlement and decantation, the sediment may be so separated and the decanted liquid may be tested in the manner

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[1] A preferable method is to keep the temperature of the water-bath at 130°F. and place water to a depth of a quarter of an inch in the air-space.

set forth in Schedule One to the Petroleum Act, 1879.

In carrying out such separation, care must be taken to minimise the evaporation of the petroleum. The separation of the sediment must not be effected by distillation.

Where the petroleum mixture is such that sediment cannot be separated by the afore-mentioned means, or where it is of a viscous nature, as in the case of indiarubber solution, quick-drying paints, &c., such mixture shall be tested in the apparatus modified as shown in the drawing hereto. This apparatus differs from that prescribed in Schedule One to the Petroleum Act, 1879, only in the addition of a stirrer to equalise the temperature throughout the sample under test.

In carrying out the test of a viscous petroleum mixture, this stirrer shall be constantly revolved at a slow speed with the fingers, except when applying the test flame, the direction of revolution being that of the hand of a clock.

With the exception of the use of the stirrer, the manner of carrying out the test shall be that set forth in Schedule One to the Petroleum Act, 1879.

The stirrer may be removed by grasping the spindle just above the blades with the finger and thumb, and unscrewing the upper sheath. The opening in the lid, through which the stirrer passes, may then be closed by a plug provided for the purpose.

When this has been done, the apparatus shall be deemed to comply with the specification set forth in Schedule One of the Petroleum Act, 1879, and may be used for testing ordinary petroleum or solid petroleum mixtures.

A model of the afore-mentioned apparatus will be deposited with the Board of Trade, and the provisions of section 3 of the Petroleum Act, 1879, in regard to verification and stamping shall apply also to such apparatus as though it were the apparatus prescribed by the said Act.

For the purpose of carrying out such verification the stirrer shall be removed and the opening plugged as hereinbefore directed. The apparatus shall then be tested with ordinary petroleum. The stirrer shall be verified by comparison of measurements.

3. *Solid petroleum mixtures.* Where the petroleum mixture is solid, as in the case of naphtha soaps, &c., the apparatus to be used for the test shall be that prescribed in Schedule One of the Petroleum Act, 1879.

The method of carrying out the test of such solid mixture shall be as follows:—

The solid mixture must be cut into cylinders 1½ inches long and ¼ inch in diameter by means of a cork borer or other cylindrical cutter having the correct internal diameter. These cylinders are to be placed in the petroleum cup of the testing apparatus in a vertical position in such number as will completely fill the cup. The cylinders must be in contact with one another, but must not be so tightly packed as to be deformed in shape.

Five or six of the cylinders in the centre of the cup must be shortened to ½ inch to allow space for the thermometer bulb.

The air bath of the testing apparatus must be filled to a depth of 1½ inches with water. The water bath must then be raised to and maintained at a temperature of about 75°F.

The cup must then be placed in the air bath, and the temperature of the sample must be allowed to rise until the thermometer in the oil cup shows 72°F., when the test flame must be applied.

If no flash is obtained, this temperature must be maintained constant in the oil cup for 1 hour, at the expiration of which time the test flame must again be applied.

If a flash is obtained, the solid mixture will be subject to the provisions of the Petroleum Acts in virtue of this Order.

Note.—It may in many cases save time in testing samples of petroleum mixtures to apply the test flame after the sample has been a few minutes in the cup and while still at the temperature of the room in which the test is being carried out, provided that this temperature is below 73°F. If a flash is obtained by this means, it is unnecessary to proceed with the test at a higher temperature.

In 1880 the subject of petroleum-testing was investigated in Germany by the direction of the Government, and a considerable number of experiments were made with different forms of apparatus. Eventually the Abel instrument was selected as the best, but exception was taken to the personal error liable to be introduced by the method of applying the test-flame, and accordingly a clockwork arrangement for moving the test-slide and bringing the igniting flame to the required position was added (Fig. 10). The clockwork movement, which is fixed to the cover of the oil cup, is wound up prior to each application of the test-flame, and is released by pressing a trigger as the mercury in the thermometer reaches each ½°C. The mechanism is so adjusted that the rate of opening and closing the test-orifice is properly timed, and the operator is therefore relieved from the necessity of timing the movement by the aid of a pendulum. The English Abel-apparatus is provided with both oil-lamp and gas arrangement for igniting the vapour, but the German instrument has the oil lamp only, as it was found that the two appliances did not give in all cases concordant results, and petroleum has advantageously been substituted for colza oil for use in the test-lamp.

Before the Abel tester had been very long in use it was found that the results afforded were materially affected by the amount of atmospheric pressure. This source of variation in flashing-point had not previously received attention, and was first accidentally observed in Germany. As the result of a series of experiments conducted in an air-tight chamber in the Jewish Hospital in Berlin at different atmospheric pressures, it was found that the difference in flashing-point amounted to about 0·30°C. for 10 mm. in the height of the barometric column, and accordingly a table of corrections was framed on this basis for use with the Abel tester in Germany. With the object of procuring some tangible evidence of the effect of barometric changes upon the flashing-point, the writer conducted, in association with Sir Frederick Abel, a series of tests at different altitudes in Switzerland, and obtained corroborative results, the observed variations in flashing-point being at the rate of 2°F. for 1 inch of barometric pressure. These experiments were, however, not made with a view of determining with precision the extent of variation, the number of tests made in the limited time being too few to justify the basing of a table of corrections on the results.

At a later date an additional source of discrepancies in the results afforded by the Abel instrument was discovered in the effect of a tropical temperature upon the liberation of vapour from the oil. The Indian Government, having adopted the Abel apparatus, had copied verbatim from the English Act the directions for applying the test, and attention was forcibly directed to the source of variations alluded to by the condemnation of several cargoes of kerosene, which had arrived in the port of Calcutta. The writer proceeded to India to investigate the matter, and as the result of experiments made in that country and of a series of tests conducted by Sir Frederick Abel and the writer, with the assistance of Dr. Kellner, in an apartment at Woolwich Arsenal heated to a tropical temperature, it was found that a much lower flashing-point than that furnished in a temperate climate was liable to be obtained when the Abel test was applied in a tropical country in the manner prescribed by the English Act. Further experiments made by Dr. Warden, analyst to the Government of Bengal, Professor Pedler of Calcutta, Dr. Lyon, Sir Frederick Abel, Dr. Kellner, and the writer, showed that the apparent depression of the flashing-point was largely due to the vapour which became disengaged in the act of filling the oil cup. Prolonged cooling of the oil appeared to reduce the liability to this disengagement of vapour, but the only practically available method of eliminating this source of discrepancies was found to be the adoption of some expedient for getting rid of the vapour before commencing the operation of testing or before the flashing-point of the oil was reached. Various methods of effecting this object were tried. The vapour was easily removed by gently blowing over the surface of the oil before placing the cover on the cup, or by the use of an aspirator attached to the cover, or by leaving the test-slide withdrawn for some time; but it was ultimately decided to recommend the commencement of the test many degrees below the flashing-point, so that the disengaged vapour might be removed by the current of air created by the test-flame in successive quantities too small to cause a flash before the active volatilisation of the oil began. With this modification in the method of applying the test in a tropical country, the apparatus is caused to give results which agree very closely with those which it furnishes in a temperate climate. Obviously, a portion of the volatile constituents of the oil becomes dissipated in this mode of conducting the test, but, since kerosene cannot be exposed to the air in the tropics without this loss occurring, the defect is not of practical importance. Further details in regard to this question will be found in a joint communication by Sir Frederick Abel and the writer published in the Chemical News on May 2, 1884. In October, 1887, Sir Frederick Abel drew up the following instructions for the use of the Abel tester in temperate and tropical climates:—

Directions for preparing and using apparatus for testing petroleum oil (these directions apply to the use of the Abel tester in temperate climates):—

1. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow pipe. The temperature of the water at the commencement of each test, as indicated by the long-bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in the vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication, or the water is heated by a spirit lamp (which is attached to the stand of the apparatus) until the required temperature is reached.

2. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton-wool moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted the flame is adjusted until it is the size of the bead fixed on the cover of the oil-cup.

3. *Filling the oil-cup.*—The oil-cup is placed on a level surface in a good light, and the oil to be tested is poured in without splashing, until its surface is level with the point of the gauge which is fixed in the cup. The oil should be poured from a suitable small vessel, never direct from a large can. The round-bulb thermometer is inserted into the lid of the cup, care being taken that the projecting rim of the collar touches the edge of the socket; the test-lamp, prepared as already described, is placed in position, and the cover put on to the cup and pressed down so that its edge rests on the rim of the cup.

4. *The application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the test-flame being compared with that of the bead on the cover. The cup is carefully lifted without being shaken, placed in the bath, and the test-lamp lighted. The thermometer in the oil-cup is now watched, and when the temperature has reached 66°F. (the sample, if necessary, having previously been cooled to below that temperature by immersing the vessel containing it in cold water), the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree.

If the oil-cup is provided with the automatic (Pensky's) arrangement for opening and shutting the slide, the clockwork is wound up by turning the knob from left to right, and set in motion by pressing the trigger.

If the slide is intended to be moved by hand, it should be drawn open slowly and shut quickly. The exact time to be observed in this operation is regulated by the swing of the pendulum supplied with this form of instrument. The opening of the slide should take the time of three oscillations, the shutting of the slide the time of the fourth oscillation of the pendulum. (By one oscillation is meant the passage of the ball of the pendulum from the greatest distance from the vertical on the one side, to the greatest distance on the other.)

If a flash occurs at the first application of the test-flame (at 66°F.), or at any point below 73°F., the operation is to be repeated with a fresh portion of the oil, which is cooled down to 55°F. before being placed in the cup. The first application of the test-flame is made when the temperature of the oil has reached 60°F.

In repeating a test, a fresh sample of oil must always be used, the tested sample being thrown away.

5. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended (see table following the directions for applying the test in hot climates), giving the flashing-points of oils ranging from 65°–80°F., under pressures ranging from 27–31 inches of mercury.

The table is used in the following manner:—

Example.—An oil has given a flashing-point of 71°, the barometer being 28·6; take the nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

The following directions apply to the use of the Abel Petroleum Tester in hot climates.

Directions for drawing the sample and preparing it for testing.

1. *Drawing the sample.*—In all cases the testing officer, or some person duly authorised by him, shall personally superintend the drawing of the sample from an original unopened tin or other vessel.

An opening sufficiently large to admit of the oil being rapidly poured or siphoned from the tin or other vessel shall be made.

Two bottles, each of the capacity of about forty fluid ounces, are to be filled with the oil. One of these, the contents of which is intended to be preserved for reference in case of need, is to be carefully corked, the cork being well driven home, cut off level with the neck, and melted sealing-wax worked into it. The other bottle may be either stoppered or corked.

2. *Preparing the sample for testing.*—About ten fluid ounces of the oil, sufficient for three tests, are transferred from the bottle into which the sample has been drawn to a pint flask or bottle, which is to be immersed in water artificially cooled until a thermometer, introduced into the oil, indicates a temperature not exceeding 50°F.

Directions for preparing and using the test apparatus.

3. *Preparing the water-bath.*—The water-bath is filled by pouring water into the funnel until it begins to flow out at the overflow-pipe. The temperature of the water at the commencement of each test, as indicated by the long bulb thermometer, is to be 130°F., and this is attained in the first instance by mixing hot and cold water, either in the bath or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or the water is heated by means of a spirit-lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

4. *Preparing the test-lamp.*—The test-lamp is fitted with a piece of cylindrical wick of such thickness that it fills the wick-holder, but may readily be moved to and fro for the purpose of adjusting the size of the flame. In the body of the lamp, upon the wick, which is coiled within it, is placed a small tuft of cotton wool, moistened with petroleum, any oil not absorbed by the wool being removed. When the lamp has been lighted, the wick is adjusted by means of a pair of forceps, or a pin, until the flame is the size of the bead fixed on the cover of the oil-cup; should a particular test occupy so long a time that the flame begins to get smaller, through the supply of oil in the lamp becoming exhausted, three or four drops of petroleum are allowed to fall upon the tuft of wool in the lamp from the dropping bottle or pipette provided for the purpose. This can be safely done without interrupting the test.

5. *Filling the oil-cup.*—Before the oil-cup is filled, the lid is to be made ready for being placed upon the cup, *i.e.* the round-bulb thermometer is to be inserted into the socket (so that the projecting rim of the collar with which it is fitted touches the edge of the socket), and the test-lamp is to be placed in position. The oil-cup, having been previously cooled by placing it bottom downwards in water at a temperature not exceeding 50°F., is now to be rapidly wiped dry, placed on a level surface in a good light, and the oil to be tested is poured in without splashing until its surface is level with the point of the gauge which is fitted in the cup. The lid is then put on the cup at once, and pressed down so that its edge rests on the rim of the cup.

6. *Application of the test.*—The water-bath, with its thermometer in position, is placed in some locality where it is not exposed to currents of air, and where the light is sufficiently subdued to admit of the size of the entire test-flame being compared with that of the bead on the cover. The cup is carefully lifted, without shaking it, and placed in the bath, the test-lamp is lighted, and the clockwork wound up by turning the key. The thermometer in the oil-cup is now watched, and when the temperature has reached 56°F. the clockwork is set in motion by pressing the trigger.

If no flash takes place, the clockwork is at once re-wound, and the trigger pressed at 57°F. and so on, at every degree rise of temperature, until the flash occurs, or until a temperature of 95°F. has been reached.

If the flash takes place at any temperature below 77°F. the temperature at which it occurs is to be recorded. The fresh portions of the sample are then to be successively tested in a similar manner and the results recorded. If no greater difference than 2°F. exists between any two of the three recorded results, each result is to be corrected for atmospheric pressure, as hereafter described, and the average of the three corrected results is the flashing-point of the sample. In the event of there being a greater difference than 2°F. between any two of the results, the series of tests is to be rejected, and a fresh series of three similarly obtained, and so on until a sufficiently concordant series is furnished, when the results are to be corrected and the average taken in the manner already described.

No flash which takes place within eight degrees of the temperature at which the testing is commenced shall be accepted as the true flashing-point of the sample tested. In the event of a flash occurring at or below 64° when the test is applied in the manner above described the next testing shall be commenced ten degrees lower than the temperature at which the flash had been previously obtained—that is to say, at 54° or thereunder, and this procedure shall be continued until the results of three consecutive tests do not show a greater difference than 2°.

If a temperature of 76°F. has been reached without a flash occurring, the application of the test-flame is to be continued until a temperature of 95°F. has been reached. If no flash has occurred up to this point, and if the petroleum is declared to be imported subject to the provisions of the Act,[1] the tests shall not be continued, and the testing officer shall certify that the petroleum has a flashing-point of over 95° and is not dangerous. But if the petroleum is oil ordinarily used for lubricating purposes, and is declared to have its flashing-point at or above 200°, or is oil to which a notification of the Governor in Executive Council exempting it from the operation of the Act will be applicable in the event of the flashing-point being found to be at or above 120°, the test shall be continued as follows:—The oil-cup is to be removed from the water-bath, and the temperature of the water in the water-bath is to be reduced to 95°F. by pouring cold water into the funnel (the hot water escaping by the overflow pipe). The air-chamber is then to be filled to a depth of 1½ inches with water at a temperature of about 95°F., the oil-cup is to be replaced in the water-bath, and the spirit-lamp, attached to the water-bath, is to be lighted and placed underneath. The test-flame is then to be again applied from 96°F., at every degree rise of temperature as indicated by the thermometer in the oil-cup until a flash takes place, or until a temperature of 200°F. or 120°F., as the case may be, has been reached. If during this operation the test-flame appears to diminish in size, the lamp is to be replenished in the manner prescribed (at 4) without interrupting the test.

If a flash occurs at any temperature between 76° and 200°F., the temperature at which it occurs, subject to correction for atmospheric pressure, is the flashing-point of the sample.

In repeating a test a fresh sample of oil must always be used, the tested sample being thrown away, and the cup must be wiped dry from any adhering oil, and cooled, as already described, before receiving the fresh sample.

7. *Correction for atmospheric pressure.*—As the flashing-point of an oil is influenced by changes in atmospheric pressure to an average extent of 1·6°F. for every inch of the barometer, a correction of the observed flashing-point may become necessary. The height of the barometer must, therefore, be determined at the time of making the test for the flashing-point. An aneroid barometer is supplied for this purpose. To facilitate the correction of a flashing-point for pressure a table is appended, giving flashing-points of oils ranging from 65° to 80°F., under pressures ranging from 27 to 31 inches of mercury.

The table is used in the following manner:—

TABLE FOR CORRECTION OF FLASHING-POINTS INDICATED BY THE TEST FOR VARIATIONS IN BAROMETRIC PRESSURE ON EITHER SIDE OF THIRTY INCHES.

Barometer in inches.																				
27·0	27·2	27·4	27·6	27·8	28·0	28·2	28·4	28·6	28·8	29·0	29·2	29·4	29·6	29·8	30	30·2	30·4	30·6	30·8	31·0
Flashing Point in Degrees Fahrenheit.																				
60·2	60·5	60·8	61·2	61·5	61·8	62·1	62·4	62·8	63·1	63·4	63·7	64·0	64·4	64·7	65	65·3	65·6	66·0	66·3	66·6
61·2	61·5	61·8	62·2	62·5	62·8	63·1	63·4	63·8	64·1	64·4	64·7	65·0	65·4	65·7	66	66·3	66·6	67·0	67·3	67·6
62·2	62·5	62·8	63·2	63·5	63·8	64·1	64·4	64·8	65·1	65·4	65·7	66·0	66·4	66·7	67	67·3	67·6	68·0	68·3	68·6
63·2	63·5	63·8	64·2	64·5	64·8	65·1	65·4	65·8	66·1	66·4	66·7	67·0	67·4	67·7	68	68·3	68·6	69·0	69·3	69·6
64·2	64·5	64·8	65·2	65·5	65·8	66·1	66·4	66·8	67·1	67·4	67·7	68·0	68·4	68·7	69	69·3	69·6	70·0	70·3	70·6
65·2	65·5	65·8	66·2	66·5	66·8	67·1	67·4	67·8	68·1	68·4	68·7	69·0	69·4	69·7	70	70·3	70·6	71·0	71·3	71·6
66·2	66·5	66·8	67·2	67·5	67·8	68·1	68·4	68·8	69·1	69·4	69·7	70·0	70·4	70·7	71	71·3	71·6	72·0	72·3	72·6
67·2	67·5	67·8	68·2	68·5	68·8	69·1	69·4	69·8	70·1	70·4	70·7	71·0	71·4	71·7	72	72·3	72·6	73·0	73·3	73·6
68·2	68·5	68·8	69·2	69·5	69·8	70·1	70·4	70·8	71·1	71·4	71·7	72·0	72·4	72·7	73	73·3	73·6	74·0	74·3	74·6
69·2	69·5	69·8	70·2	70·5	70·8	71·1	71·4	71·8	72·1	72·4	72·7	73·0	73·4	73·7	74	74·3	74·6	75·0	75·3	75·6
70·2	70·5	70·8	71·2	71·5	71·8	72·1	72·4	72·8	73·1	73·4	73·7	74·0	74·4	74·7	75	75·3	75·6	76·0	76·3	76·6
71·2	71·5	71·8	72·2	72·5	72·8	73·1	73·4	73·8	74·1	74·4	74·7	75·0	75·4	75·7	76	76·3	76·6	77·0	77·3	77·6
72·2	72·5	72·8	73·2	73·5	73·8	74·1	74·4	74·8	75·1	75·4	75·7	76·0	76·4	76·7	77	77·3	77·6	78·0	78·3	78·6
73·2	73·5	73·8	74·2	74·5	74·8	75·1	75·4	75·8	76·1	76·4	76·7	77·0	77·4	77·7	78	78·3	78·6	79·0	79·3	79·6
74·2	74·5	74·8	75·2	75·5	75·8	76·1	76·4	76·8	77·1	77·4	77·7	78·0	78·4	78·7	79	79·3	79·6	80·0	80·3	80·6
75·2	75·5	75·8	76·2	76·5	76·8	77·1	77·4	77·8	78·1	78·4	78·7	79·0	79·4	79·7	80	80·3	80·6	81·0	81·3	81·6

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[1] The Indian Petroleum Act is here referred to.

Example.—An oil has given a flashing-point of 71°, the barometer being at 28·6; take the nearest number to 71° in the vertical column headed 28·6. This number is 70·8. Substitute for this the number in the same horizontal line in the column headed 30 (the normal height of the barometer). The substituted number, *i.e.* the true flashing-point of the oil, is 73°.

'Dangerous petroleum' is defined by the Indian Petroleum Act as 'petroleum having its flashing-point below 76° of Fahrenheit's thermometer. Provided that, when all or any of the petroleum on board a ship, or in possession of a dealer, is declared by the master of the ship or the consignee of the cargo, or by the dealer, as the case may be, to be of one uniform quality, the petroleum shall not be deemed to be dangerous if the samples selected from the petroleum have their flashing-points, on an average, at or about 73° of Fahrenheit's thermometer, and if no one of those samples has its flashing-point below 70° of that thermometer.'

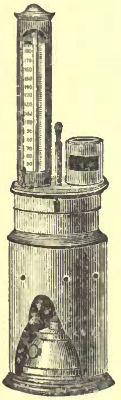

FIG. 11.

The Abel apparatus, with a standard of 22°C., was in 1885 adopted as the legal test in Sweden, and in the year 1888 a Bill was introduced in the Danish legislature to substitute the Abel tester with a standard of 23°C., for the open tester, with a standard of 40°C., then in use in Denmark. In Russia the standard with the Abel-Pensky instrument is 28°C.

The Abel tester is by no means the only form of closed testing apparatus at present in use, and, in addition to those actually employed, a large number of instruments on the closed-cup principle have been devised. Many years ago Tagliabue, of New York, introduced an apparatus (Figs. 11 and 12) with a covered brass oil cup communicating by means of a spring valve with a dwarf chimney. The opening of the valve and the simultaneous introduction of a flame into the chimney determines a current of air through the upper part of the oil-cup which sweeps out the inflammable vapour and brings it into contact with the flame. Tagliabue also constructed a larger instrument of the same form with a glass oil-cup. The Michigan and Wisconsin States tester has a copper oil cup with a copper cover provided with a small orifice to which the test flame is applied. The New York State tester, devised by Elliott, has a glass oil-cup of comparatively large size with a convex glass cover. Parrish's naphthometer (Fig. 13) is provided with a stationary test flame fed by the oil in the testing cup, and Foster's automatic tester (Fig. 14) is similar in principle. In Millspaugh's closed tester (Fig. 15) the oil-cup is of glass and is immersed only to the extent of one-tenth of its depth in the water-bath, with the object, apparently, of preventing the overheating of the surface of the oil. Mann's tester (Fig. 16) represents an attempt to reproduce in the testing apparatus the conditions prevailing in an ordinary petroleum lamp, the burner of the lamp being replaced by a tube, the stopper of which is blown out when, upon the introduction of a light through a lateral opening, ignition of the vapour occurs. In Pease's closed tester (Fig. 17) the vapour is ignited by an electric-spark. The writer remembers seeing, about the year 1870, a closed tester, with electric-spark igniting arrangement, in use by Dr. Letheby in his laboratory at the London Hospital. The

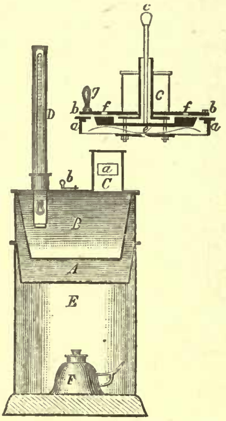

FIG. 12.

The smaller illustration represents in section the cover of the instrument shown in Fig. 11. *a, a.* Cover. *b, b.* Movable bar, with openings *f, f,* closed by the bar *e*, beneath which is a spring. *c.* Rod to depress the bar *e*, and thus uncover the openings *f, f.* *g.* Handle to move the bar *b, b.* C. Hood with opening for insertion of flame.

The larger illustration represents in section a simpler form of the instrument. A. Water-bath. B. Oil-cup. C. Hood, with opening *a.* D. Thermometer. E. Lamp furnace. F. Lamp. *b.* Pivoted cover, closing orifice beneath it.

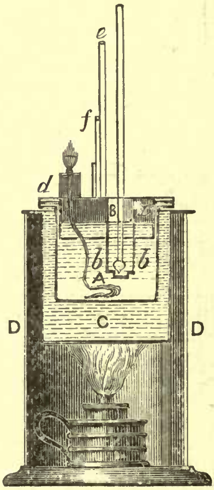

FIG. 13.

A. Oil-cup. C. Water-bath, D. Lamp-furnace. *e.* Screen, with glass plate *f.* B. Chamber communicating with the air, with openings *a* (for circulation of air) and *b, b* (to allow passage of oil from B into A). *d.* Cylinder supporting a small wick for test flame.

oil-cup was of glass, with a hinged metal cover, which was blown open when the vapour ignited. In 1882, Braun, of Berlin, patented a magnetic pendulum arrangement for applying the test flame in the Abel apparatus. In 1881, Engler and Haas made a number of experiments with the Abel apparatus and other testing instruments, and expressed the opinion that the addition of an arrangement for agitating the oil was desirable; Victor Meyer, however, previously proposed the addition of a stirrer. Owing to the facts that in the use of the Abel tester a layer of vapour of gradually increasing thickness is formed upon the surface of the oil and that the temperature of the oil is not uniform throughout, it is, no doubt, necessary that the dimensions of the air space above the oil, the depth to which the test-flame is inserted, the size of the test-flame, the size of the orifices in the cover, the position of the thermometer bulb, and other particulars, should be defined with greater accuracy than would probably be necessary if a stirrer were added, but experience has shown that the Abel apparatus can be readily standardised, and any number of instruments can thus be constructed to give concordant results if used with a reasonable amount of care. The apparatus known as the Engler tester (Fig. 18) consists of a copper water-bath surmounted by a second water-bath of glass supporting a glass oil-cup with brass cover in which are two semi-circular openings with hinged lids. Two insulated wires in connection with a small induction coil terminate in platinum points 1 mm. apart at a distance of ½ to ⅝ cm. from the surface of the oil, and in the centre of the oil-cup is a paddle stirrer attached to a spindle passing through the cover. Beneath the lower water-bath a spirit lamp is placed, and, as the temperature approaches the flashing-point of the oil, the spark is passed at each degree rise in the thermometer, care being taken that the passage of the spark is continued from half to one second. After each application of the spark the oil is gently agitated by rotating the stirrer. When the ignition of vapour occurs the hinged flaps are thrown open. It is claimed that by the use of the double water-bath and the stirrer the heating is rendered slow and regular, and as far as possible independent of the size of the heating flame; also that by the employment of the electric spark, the size, intensity, and distance of the igniting agent from the oil are rendered uniform. Moreover, that the extraneous formation of vapour through the heating of the surface of the oil which may take place when an ordinary test-flame is employed cannot occur in the use of the electric spark as described. Finally it is contended that the

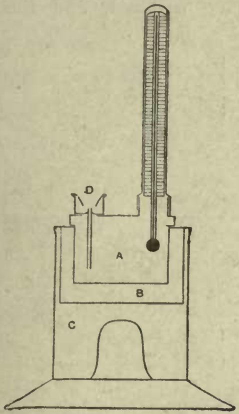

FIG. 14.

A. Oil-cup. B. Water-bath. C. Jacket. D. Flash-jet.

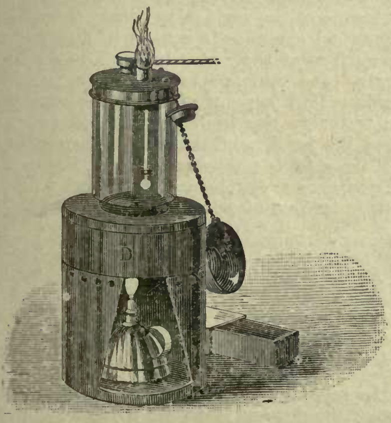

FIG. 15.

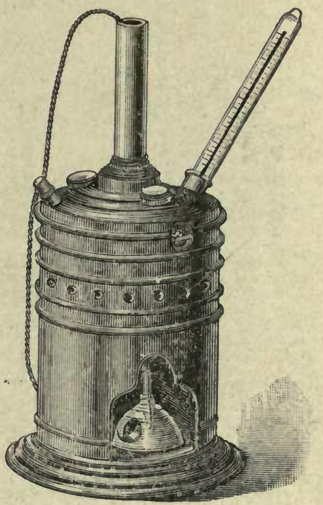

FIG. 16.

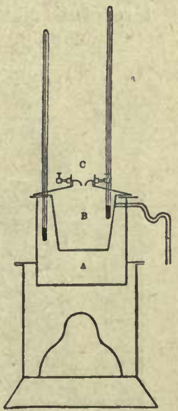

FIG. 17.

A. Water-bath. B. Oil-cup. C. Spark wires.

conditions prevailing in a petroleum lamp are reproduced to a large extent in the Engler tester.

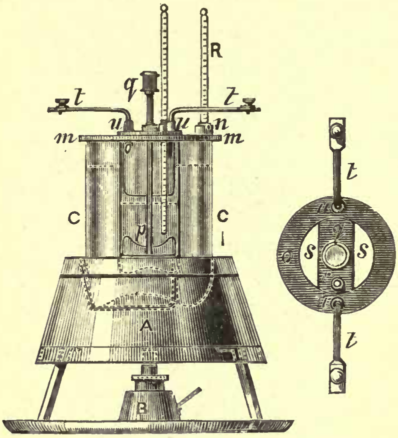

FIG. 18.

A. Copper water-bath. B. Spirit lamp. C, C. Glass water-bath, with filling mark etched upon it. *m, m.* Cover. R. Thermometer, supported in the water by collar *n.* *o.* Glass oil-cup, with filling mark. *s, s.* Openings with hinged covers. *t, t.* Conducting wires, insulated by ebony rings *u, u,* and terminating in platinum points. *p.* Stirrer, with handle *q.* *r.* Thermometer in the oil.

Among other systems of testing are those of Liebermann, Beilstein, and Stoddard, which are based upon the principle of blowing air at intervals through a jet plunged beneath the surface of the oil, contained in a vessel in which it can be gradually heated, until inflammable vapour is evolved. In Bernstein's tester (Fig. 19) the level of the oil is raised from time to time, as the temperature of the oil increases, until vapour issues from the oil chamber and ignites at a stationary flame, and in the Ehrenberg tester a syringe is employed to expel the vapour from the closed oil chamber and bring it into contact with a flame.

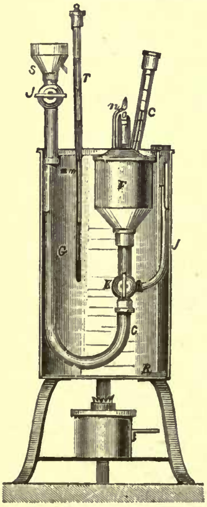

FIG. 19.

There yet remains to be noticed a form of petroleum testing apparatus, which has been employed to some extent in France, in which the flashing-point is deduced from the vapour tension. This apparatus, known as the Salleron-Urbain tester (Fig. 20), consists of a closed metallic vessel AA, in the cover of which are inserted a cylindrical chamber B, a regulating screw *r,* a graduated tube *m,* 35 cm. in length, and a thermometer. The cylindrical chamber is closed at the top by a screw-plug *p,* and at the bottom by a sliding plate, which cuts off communication between the chamber and the vessel below. 50 c.c. of water having been placed in the lower vessel, the cylindrical chamber is nearly filled with the petroleum to be tested, the screw-plug replaced, and the apparatus placed in warm water until the temperature has become constant. The water-level in the graduated tube having been adjusted to zero by means of the regulating screw, the oil in the cylindrical chamber is caused to flow out upon the surface of the water in the lower vessel by moving the sliding plate. The expansion of the liberated vapour of the petroleum causes the water to rise in the graduated tube, and, when the level is stationary, its height is read off. In a table published in 1866, Salleron and Urbain give the following figures of sp.gr. and vapour tension of petroleum at 15°:

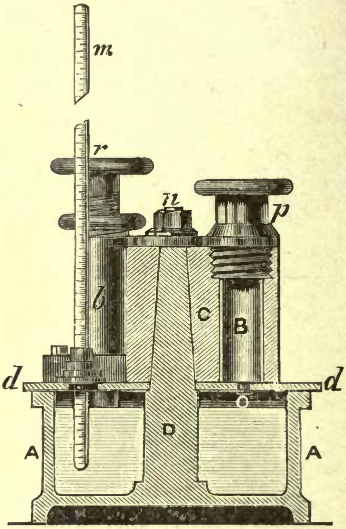

FIG. 20.

Density at 15°C.	Tension in mm. of water	Density at 15°C.	Tension in mm. of water
0·812	0	0·756	125
0·797	5	0·735	410
0·788	15	0·695	930
0·772	40	0·680	1185
0·762	85	0·650	2110

In regard to the Salleron-Urbain system of testing, Engler and Haas remark that the method depends upon the assumption that the numbers which express the expansion of the petroleum vapour run parallel with the temperature of the inflammability of all kinds of petroleum; but that the supposition is found not to be correct in all cases, inasmuch as the presence of a small quantity of very volatile hydrocarbons[1] occasions an increased pressure in the apparatus. The general conclusion is, however, expressed that oils which exhibit a tension of not more than 64 mm. of water at 35° may be considered safe.

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[1] Presumably a quantity too small to sensibly affect the inflammability.

In a report to the New York State Board of Health in 1882, Professor Arthur H. Elliott records the particulars of a large number of experiments with various forms of testing apparatus, and gives the following table of comparative results :—

Oil used.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
	Flashing-points, F.										
No. 1 . . .	110°	118°	120°	111°	117°	107°	103°	130°	111°	95°	119°
No. 2 . . .	111°	121°	124°	115°	118°	109°	102°	128°	107°	96°	—
No. 3 . . .	119°	122°	122°	112°	118°	108°	102°	130°	108°	95°	118°
No. 4 . . .	97°	96°	97°	90°	93°	86°	76°	90°	81°	75°	96°

I. Tagliabue (open cup). II. Arnaboldi (open cup). III. Saybolt. IV. Tagliabue (closed cup—small). V. Tagliabue (closed cup—large). VI. Wisconsin State. VII. Abel. VIII. Bernstein. IX. Millspaugh. X. Mann. XI. Foster.

From the statements which have been made it will be evident that there is a regrettable absence of uniformity in the methods of testing adopted, not only in different countries, but also in the various States of the American Union. The existence of considerable diversity in regard to the test standard to be adopted with any one system of testing is also exhibited in the laws which have been framed in the United States. The latter condition no doubt arises from the fact that, at the outset, no systematic attempts were made to determine the relation between the flashing-point of an oil and its safe or dangerous character in ordinary use.

(*e*) *Burning quality.*—The testing of the burning quality of kerosene is regularly effected in well-conducted refineries in the United States by burning the oil in lamps of the usual construction and noting the diminution in the size of the flame which occurs in a stated period. The results are, however, dependent upon so many variable conditions that attempts have been made to substitute a test of greater precision ; but beyond the improvement of the existing test, the efforts made have not been attended with success. The Saybolt lamp (Fig. 21), specially constructed for testing purposes, consists of a tall glass cylindrical graduated reservoir of small diameter, with a burner which furnishes a well-shaped flat flame of considerable height in proportion to the width, a wick carefully selected for the purpose, and a graduated glass chimney. The lamps are burned in water at 60°F., the diminution in the height of the flame and the depression of the oil level being noted.

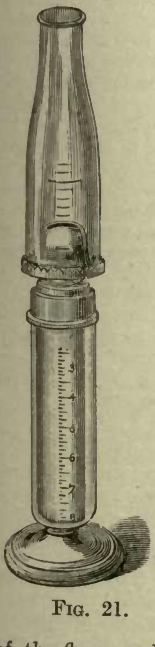

Fig. 21.

In Canada the ' burning percentage ' is determined by the use of a lamp thus described : ' The bowl of the lamp is cylindrical, 4 in. in diameter and 2¾ in. deep, with a neck placed thereon of such a height that the top of the wick tube is 3 in. above the bowl. A sun hinge burner is used, taking a wick ⅞ in. wide and ⅛ in. thick, and a chimney about 8 in. long.' The test is conducted as follows : ' The lamp bowl is filled with the oil and weighed, then lighted and turned up full flame, just below the smoking point, and burned without interference till 12 oz. of the oil is consumed. The quantity consumed during the first hour and the last hour is noted.' The ratio of the two quantities is the measure of the burning quality, and the percentage that the latter quantity is of the former is the ' burning percentage ' referred to.

The writer has devoted much time to the perfecting of a system of testing burning quality with lamps of the usual construction, and has succeeded in eliminating some of the sources of discrepancies in the results afforded. Obviously the wick used should be carefully chosen, and, as a fresh wick should be employed for each test, it is important that the wick should be examined before use, and any defective portion rejected. In standardising the wick and verifying its uniformity, the writer has found it advantageous to determine the quantity of a mineral oil of known quality drawn out of a vessel under definite conditions as to temperature, &c., by the capillary attraction of a piece of the wick arranged as a syphon (Fig. 22). In all cases the wick must be dried immediately before use and immersed in the oil while still warm. The oil chambers of the lamps employed must be of uniform dimensions, and the burners must first be tested to ascertain that they furnish similar flames with the same oil. The wick must be trimmed with scrupulous care before the lamp is lighted, and the oil in the lamp must be maintained at a constant temperature—that of 60°F. being a desirable one. The wick should be raised so as to obtain a flame of the largest size possible without the production of smoke. For recording the size and shape of the flame at the commencement of the experiment and the diminution in size and alteration in shape of the flame at intervals during the progress of the test, the writer has found it convenient to employ a camera by means of which the outline of the flame may be traced on thin paper at intervals (Fig. 23). No general agreement has, however, yet been arrived at as to the extent of diminution which shall, under the specified conditions, be permissible with oils to be classed as of satisfactory burning quality. In doubtful cases several tests of the sample should be made, as the results appear to be sometimes affected by causes not well understood. In consequence of the difficulty of devising a thoroughly satisfactory method of testing oils by burning, it has been proposed to establish a distillation test, the inferiority in burning quality being supposed to arise from the oil not being of natural composition or from its containing too large a percentage of the denser hydrocarbons. Attempts in this direction have not, however, been attended with success, oils of different burning quality furnishing in some cases similar results, and oils of equally good burning quality sometimes giving dissimilar results on fractional distillation. The testing of the oil under conditions as nearly as possible approaching to those under which it is practically used appears to be the most rational method of determining the burning quality, and is no doubt the best in the absence of any arbitrary test capable of being easily and expeditiously applied and of furnishing trustworthy results. The viscosity of the oil has been found in some cases to afford a useful indication of burning quality.

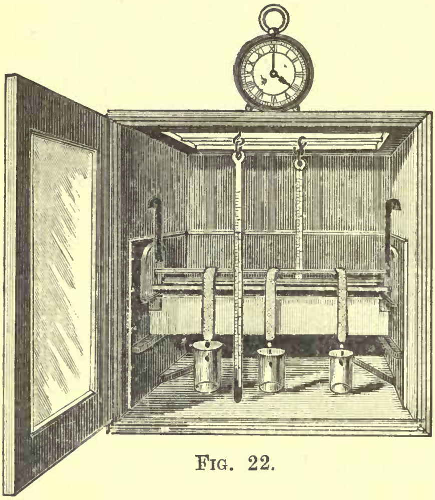
FIG. 22.

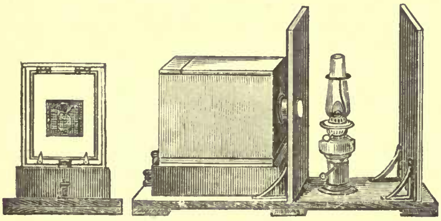
FIG. 23.

Kerosene oil should bear agitation with oil of vitriol without material darkening of colour, and warm water shaken with it should exhibit neither markedly alkaline nor even faintly acid reaction, and should give no precipitate with barium chloride solution. Upon being distilled, kerosene should not evolve sulphurous acid. If the presence of any considerable amount of sulphur compounds is suspected, the oil should be burned in a Referee's gas-testing apparatus, or in the Mahler bomb, and the sulphur products estimated as barium sulphate.

4. *Lighthouse oil.*

The Trinity House contract conditions for mineral oil intended for use in lighthouse lamps specify that—

(1) The mineral oil required to be supplied under this contract is to be of the best possible quality, the greatest care is to be taken in its preparation, and it must be perfectly free from sulphuric acid.

(2) In all cases, whether the oil be petroleum or paraffin, its flashing-point is to be determined by using the apparatus described in Schedule 1 of the Petroleum Act of 1879.

(3) If the oil be petroleum, its flashing-point is to be not lower than 125°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(4) If the oil be paraffin, its sp.gr. is to be not less than 0·810, nor greater than 0·820, at 60°F.; its flashing-point is to be not lower than 140°F. (close test), and it is to distil between 302° and 572°F., the temperature of the vapour, not that of the liquid, being taken.

(5) The illuminating power of the oil supplied, whether petroleum or paraffin, is to be equal to that of the best colza oil when consumed in a Trinity House Argand lamp.

For the distillation test about 250 grams of the oil may be taken, the operation being conducted in an ordinary distillation flask with the bulb of the thermometer midway between the shoulder of the flask and the lateral tube leading to the condenser. The upper part of the flask should be wrapped in asbestos cloth.

The United States Lighthouse establishment stipulates that mineral oil supplied for use in lighthouse lamps shall have a sp.gr. 'not less than 0·802,' a flashing-point of not less than 140°F., and a fire-test of not less than 154°F., both these tests being made with Tagliabue's instrument. The oil is to remain limpid at zero; and 'litmus paper immersed in it for 5 hours must remain unchanged.' The oil is to be photometrically tested in a fifth-order Hains lamp, and the light is to be equal to that of eighteen sperm candles, and to continue undiminished during 5 hours' burning.

5. *Lubricating oils.*

a. Colour. In the case of what are known as pale oils, the trade are accustomed to take exception to any marked increase in the ordinary depth of colour, but as yet there are no accepted standards of colour for these oils, such as have been fixed for kerosene. The writer has, however, for some years past, used the instrument (Fig. 24) known as Lovibond's Tintometer[1] in ascertaining and recording the colour of a two-inch column of lubricating oils, and comparative results have thus been furnished for the guidance of the trade.

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[1] This instrument, devised by Mr. Joseph W. Lovibond, of Salisbury, consists of a covered trough or box divided longitudinally by a partition terminating in a vertical knife-edge opposite an eye-piece fixed at one end, and forming two channels slightly diverging from the end at which the eye-piece is placed. In one channel the liquid to be examined, which is contained in a rectangular glass cell, is placed; and in the other channel numbered slips of coloured glass, of known depth of tint, are inserted.

b. Odour. Lubricating oils should be free from empyreumatic odour, as the presence of such odour would indicate that the process of refining had not been satisfactorily carried out.

c. Specific gravity. Mineral lubricating oils of similar description were formerly graded solely with reference to specific gravity, but, experience having shown that the density is not necessarily an index of the lubricating value, it is now generally recognised that specific gravity is of less importance than viscosity.

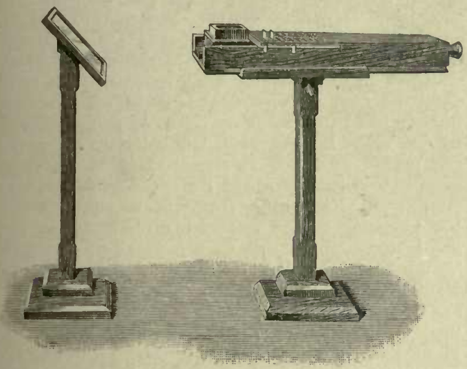

FIG. 24.

d. Flashing-point and fire-test. In the determination of the flashing-point by the closed and open tests, and for the determination of the fire-test, the writer is accustomed to use an instrument made by Pensky of Berlin. In its closed form this apparatus resembles in principle the Abel tester employed in the examination of kerosene. The water-bath is, however, replaced by an air-bath, consisting of a thick cast-iron vessel which is heated by a Bunsen burner, and the application of the gas test-flame is effected through the medium of a revolving vertical spindle with a non-conducting cap, which can be grasped by the finger and thumb without inconvenience even when the apparatus is used at high temperatures. In the use of this instrument the flame of the burner should be adjusted so that the temperature of the oil rises at the rate of about 10°F. per minute. The latest form of the apparatus, known as the Pensky-Martens tester (Fig. 25), is provided with a revolving stirrer which agitates the atmosphere above the oil as well as the oil itself.

If the cover of the oil-cup be removed, the apparatus referred to may be employed for the determination of the open-vessel flashing-point and the fire-test, a gas flame, not more than ¼ inch in diameter, being used to produce the ignition.

Inspectors of lubricating oils in the United States commonly use in ascertaining the fire-test an open metallic cup, supported on a tripod stand and heated directly by the flame of a spirit lamp, the temperature being raised at the rate of eight degrees Fahrenheit per minute.

In some cases it is customary to test the volatility of the oil by noting the loss of weight sustained by a given quantity of the oil when exposed for a specified length of time in a shallow vessel to an elevated temperature. The oil is sometimes absorbed by filter-paper before exposure to heat.[1]

e. Cold-test. The method in which the 'cold-test' of lubricating oils is made varies with the description of oil, and to some extent with the interpretation which the operator places on the term. The cold-test of pale oils is usually accepted as being the point at which on a gradual reduction in the temperature separation of solid hydrocarbons commences. To some descriptions of pale lubricating oils the following 'cold-test,' which may be termed the 'cloud-test,' is applied in the writer's laboratory: A beaker about 3 ins. in height by $1\frac{1}{2}$ ins. in diameter, is filled to a depth of 1 in. with the oil to be tested. The oil is slowly cooled, and from time to time is gently stirred with a thermometer until the first indication of the separation of paraffin is observed. This indication often takes the form of a cloudy stream following the thermometer as it is slowly moved. Some of the more viscous pale oils contain hydrocarbons which are not very crystalline, resembling vaseline rather than paraffin wax, and the point at which these hydrocarbons begin to separate under the influence of cold is not easily determined. In some of such cases it is preferable to take the point at which the oil becomes reduced to a semi-solid consistency or ceases to flow on inclining the vessel in which

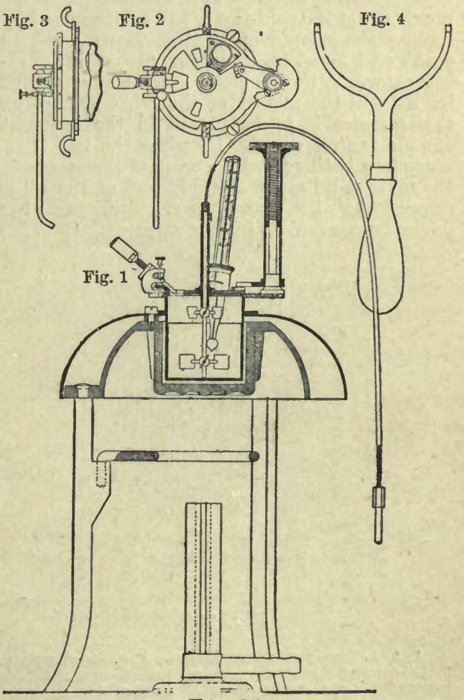

FIG. 25.

Fig. 1. Apparatus with test-flame in position for igniting the vapour. Fig. 2. Cover of oil-cup. Fig. 3. Side view of cover. Fig. 4. Handle for removing oil-cup from bath when hot.

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[1] The writer is accustomed to expose 25 grams for 12 hours in a shallow dish to a temperature of 150°F. in the case of spindle and engine oils, and 250°F in the case of cylinder oils.

it is contained. In all cases it is important that the temperature of the bath employed for cooling should not be much lower than that at which the separation, or solidification, occurs, and it is therefore desirable to determine approximately the cold-test by a preliminary operation. Where the separation of solid hydrocarbons is well defined, the test may be made in a tube about 1 in. in diameter, containing about 1½ ins. in depth of oil in the following manner: Plunge the tube into a vessel of iced water, or, if necessary, into ice and salt, until a thin layer of paraffin congeals on the sides, stirring the oil with a thermometer while the reduction of temperature is being effected. Take out the tube, wipe it, and holding it between the operator and the window, stir the contents with a thermometer until the last traces of paraffin have disappeared, when the temperature is to be noted. Repeat the experiment, again noting the temperature. Make a third test, and if the results of the last two experiments agree, record this temperature as the cold-test of the sample.

Black oils are tested by cooling them until they cease to flow, as the commencement of the separation of solid hydrocarbons cannot be observed in these oils.

The rules of the New York Produce Exchange provide that the cold-test is to be determined by cooling the sample in a glass vessel, 4 ins. in depth and 3 ins. in diameter, placed in a refrigerator. A thermometer is to be placed with its bulb in the middle of the oil, and another thermometer is to be placed in the ice-chest outside the oil vessel. If, when the two thermometers both record a specified temperature, the oil is still limpid, the cold-test of the oil is deemed to be satisfactory. Tagliabue has devised a convenient form of apparatus (Fig. 26) for the application of this test, the oil-cup being supported on a rocking bar in a jacketed cooling-chamber with a glass window. In practice, however, the cold-test is usually determined by cooling the oil in a glass cylinder 1⅝ in. in diameter.

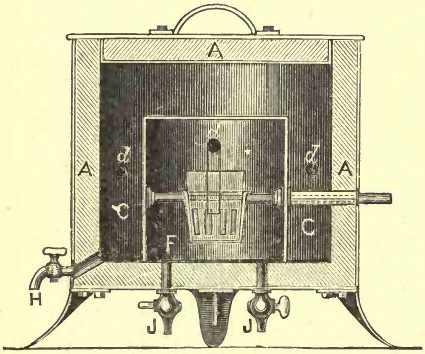

FIG. 26.

A, A, A. Non-conducting jacket. C, C. Ice-chamber. F. Oil-cooling chamber, inclosing the oil-cup, which is supported on a rocking-shaft. H. Tap for draining ice-chamber. J, J. Stop-cocks, through which warm air may be forced when it is desired to raise the temperature in F. *d*, *d*, *d*. Thermometers; the central one having its bulb in the oil.

f. Viscosity. It has been already stated that this test has become recognised as the proper basis for the grading of lubricating oils, and has accordingly become of considerable importance. The test is necessarily an arbitrary one, and there is at present no universally accepted method of testing and expressing the results, though in this country the Redwood viscometer has been adopted by the Admiralty, the War Department, the principal railway companies, the Scottish Mineral Oil Association, and the petroleum trade generally. The simplest form of instrument available for the determination of viscosity consists of a glass pipette filled to a mark on the neck and allowed to discharge its contents, the relation between the period occupied in the outflow of a given sample and that required for the discharge of a similar quantity of a standard oil expressing the viscosity of the former sample in terms of the latter. The standardising of glass pipettes is, however, difficult, since the results are affected by the form of the constricted portion of the tube, apart from the size of the orifice, and two pipettes standardised with an oil of a certain viscosity may not afford concordant results with an oil of very different viscosity. Moreover, the maintenance of the required temperature of a sample contained in a glass pipette cannot always be satisfactorily effected. For these reasons the jacketed glass viscometers of Veitch-Wilson, MacIvor, and Sacker have not been found to afford sufficiently accurate results.

The Saybolt viscometer, in its original form (Fig. 27), is provided with an oil vessel of comparatively large diameter placed in a water-bath of considerable capacity. The viscometer jet is of metal, and is inclosed in a tube extending below the orifice. Immediately above the jet the oil vessel is much contracted in diameter, and a portion is cut away on each side so as to expose an inner glass tube. At a corresponding level, glass windows are inserted in the water-bath. Round the upper part of

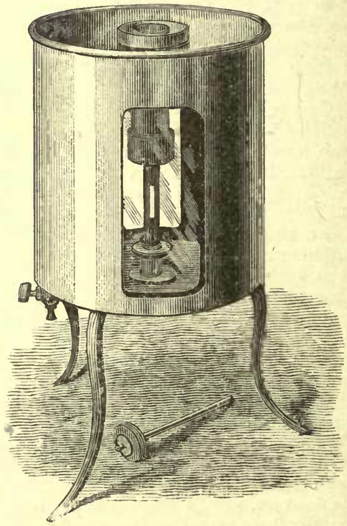

FIG. 27.

the oil-vessel is fitted an oil-tight gallery with raised edge, and above the platform of the gallery the oil-cylinder is pierced with a number of small holes. In the use of the apparatus, the bath is filled with water at the required temperature, and, a cork having been inserted in the mouth of the tube inclosing the jet, the oil-vessel is filled with the oil to be tested, until overflow through the orifices referred to occurs. The oil is then stirred with a thermometer, the gallery taking the overflow, and its temperature adjusted if necessary. On withdrawing the thermometer, oil passes from the gallery into the oil-vessel to replace that which had overflowed on the insertion of the instrument. The gallery is then emptied by means of a pipette, the length of the oil column being thus determined by the position of the circle of holes; the flow of oil from the jet is started by the withdrawal of the cork from the outer tube; a stop-watch is concurrently set in motion, and the operator, looking through the window in the water-bath and through the glass tube forming the lower part of the oil-vessel, stops the watch when the oil-level makes its appearance.

The Arvine viscometer for testing cylinder oils consists of a copper tube of small diameter coiled in a bath in which water is kept in a state of ebullition. At its lower end the tube is furnished with a small stop-cock, forming a jet, and at its upper end with a funnel to hold the oil.

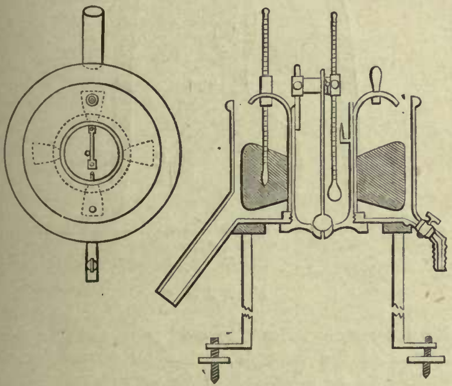

Fig. 28.

The Redwood viscometer (Fig. 28) is a modification of the instrument formerly used at the Battersea Works of Price's Patent Candle Company. It consists of a silvered copper oil cylinder, about 1⅞ ins. in diameter and 3½ ins. in depth, furnished with an agate jet fitted into a slightly conical metal seating. The cylinder is fixed in a brazed copper water-bath provided with a copper heating-tube projecting at an angle of 45° from the side near the bottom, as well as with a revolving agitator carrying a curved shield to prevent splashing, and a thermometer to indicate the temperature of the liquid in the bath. The oil cylinder has a stopper consisting of a small brass sphere which rests in a hemispherical cavity in the agate jet. The sphere is attached to a wire by means of which it is raised and suspended from a standard which supports a thermometer in the oil. Inside the oil-cylinder, and at a short distance from the top, is fixed a small bracket terminating in an upturned point, which serves as a gauge of the height to which the cylinder is filled. The instrument is supported on a tripod stand. Great care is taken in the construction of the agate jets to secure uniformity, and any slight differences in the rate of flow are corrected by slightly altering the position of the pointed bracket in the oil-clyinder. The instruments are thus all standardised. The viscometer is used in the following manner:—The bath is filled with a suitable liquid to a height corresponding with the point of the bracket in the oil-cylinder. Water may be used for temperatures up to 200°F., and a heavy mineral oil for higher temperatures. The liquid being at the required temperature, the oil to be tested, which may previously be brought to the same temperature, is poured into the inner cylinder until its level just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop-watch at the same time started, and the number of seconds occupied in the outflow of 50 c.c. noted. When oils are being tested at a temperature much above that of the laboratory, a gas flame is applied to the heating tube, and the agitator kept in gentle motion throughout the experiment. The maintenance of the exact required temperature of the oil is thus, after a little practice, rendered easy. It is important that the apparatus should stand perfectly level, and that the oil should be free from dirt, water, or other suspended matter. The writer is accustomed to express the results in terms of the viscosity of rape oil at 60°F., correcting for differences in specific gravity. Accordingly the number of seconds occupied in the outflow of 50 c.c. of the oil under examination is multiplied by 100 and divided by 535 (the average time occupied in the outflow of 50 c.c. of rape oil at 60°F. according to the writer's experiments). The result is then multiplied by the sp.gr. of the oil under examination, at the temperature of the experiment, and divided by 915 (the sp.gr. of refined rape oil at 60°F.).

The writer has devised a modified form of his viscometer, which, with the authority of the Admiralty, will be known as the Admiralty type for testing oil fuel. This instrument, as the name indicates, has been specially constructed for use in determining the viscosity of oil fuel, for contract purposes, and is intended to be employed at a temperature of 32°F. The oil-vessel is of the same dimensions as that of the original instrument, but the agate jet is longer and of larger bore, the new viscometer being designed to give an outflow in one-tenth of the time occupied in the outflow of a similar volume from the original pattern. The jet is so mounted as to be completely surrounded by the water in the bath. The water-bath, which is of comparatively large size, and is jacketed, has no lateral heating-tube, but is provided with the usual rotating stirrer. The design is registered, and the sole makers are Messrs. Baird & Tatlock (London), Limited. The oil to be tested should be subjected to prolonged cooling at 32°F. by being kept in a refrigerator through the night, or for at least six hours, immediately before being placed in the oil-cup, and should be thoroughly stirred before being transferred to the oil-vessel, and when accurate results are required the viscometer should be placed in a refrigerating chamber, the temperature of which is maintained at 32°F.

The Engler viscometer, which is largely used in Germany, is constructed on the same principles as the foregoing, the viscosity of the oil being compared with that of water. The following description of the instrument is taken from the writer's 'Petroleum and its Products' (Griffin), 2nd. ed., 602, 603 :—

The apparatus (Fig. 28A) is provided with an oil-cup, A, of brass, closed by a lid, A_1. The oil-cup is of the dimensions given in the figure, and its inner surface is gilt. In the centre of the convex bottom of the oil-cup is an outflow-tube, *a*; of platinum (brass being attacked by the oil after being some time in use) 20 mm. long and 2·9 mm. internal diameter at the top, decreasing to 2·8 mm. at the outlet. This tube can be closed by a pointed rod, *b*, of hard wood, introduced through the lid of the cup. Three small pointed studs, *c*, turned up at right angles, on the walls of the cup, serve to indicate the surface-level of the oil, marking a capacity of 240 c.c., and also show whether the apparatus is properly adjusted as regards level. A thermometer, *t*, is inserted in the lid to register the temperature of the oil. The oil-cup is fixed in an open oil-bath, B, containing a thermometer, t_1. The oil-bath is supported by a tripod stand, and is heated by means of a ring burner. A measuring-glass, C, marked at 200 c.c. and at 240 c.c., is placed exactly below the pipe, *a*.

To ensure the attainment of satisfactory results, the dimensions given must be strictly adhered to, for, although the error caused by altering some of them can be corrected, so far as the flow of water at 20°C. is concerned, by varying the length of the pipe, *a*, the correction is of no value for oils at other temperatures, and the difference in result between such instruments and one of standard dimensions increases with the viscosity of the oil tested.

Every instrument, even when standardised, should be tested before using the first time, and again after having been some time in use, by carefully rinsing out the cup with ether, alcohol, and water, in succession carefully drying the outflow pipe with a strip of filter paper, and observing the time required for the outflow of 200 c.c. of water maintained at 20°C. The water should be quite free from any rotary motion before the vent peg is withdrawn. The time should be 51–53 seconds, and the test should be twice repeated. The difference should not exceed 0·5 second, and the decimals of the average are counted as one second. To test oils, the cup must be most carefully cleansed of all damp and dirt, rinsed with alcohol, ether, and petroleum in succession, and then filled with the oil up to the gauge points. The oil having been brought to the desired temperature by heating the oil-bath, and maintained at that point for 2 or 3 minutes, the peg is withdrawn, and the outflow timed by a good chronometer. The result in seconds, divided by the rate for water at 20°C., gives the viscosity of the oil, *e.g.*—

Rate of flow of oil, 276 seconds.
„ „ water at 20°C., 53 seconds.
Result=5·2.

Oil containing suspended particles, solid matter, or water, must be filtered or dried before testing.

It has been already stated that in expressing the results obtained with the Redwood viscometer a correction is made for differences in sp.gr. As far as the writer is aware, the first published suggestion of an arrangement for eliminating differences due to sp.gr. was made by Prof. W. P. Mason, of Troy, N.Y., who described in the Chem. News for Oct. 31, 1884, an apparatus for determining viscosity, and proposed that the length of the column of the oil to be tested should be so adjusted as to be inversely proportional to the sp.gr., and maintained at this calculated length during the outflow of the standard quantity. Mr. Napier, of Glasgow, appears, however, to have previously suggested the reduction of the observed viscosity of an oil to a standard density. In the instrument proposed by Mr. Napier the oil cylinder was in two parts, connected by a flexible tube, the upper part being supported in such a manner that it could be placed at a given point on a fixed scale, the height being determined by the sp.gr. of the oil. The movable part of the oil vessel was provided with an overflow pipe, and by the use of a reservoir with a stopcock it was intended to produce a continuous slight overflow, so that the oil-level should be maintained at a fixed point.

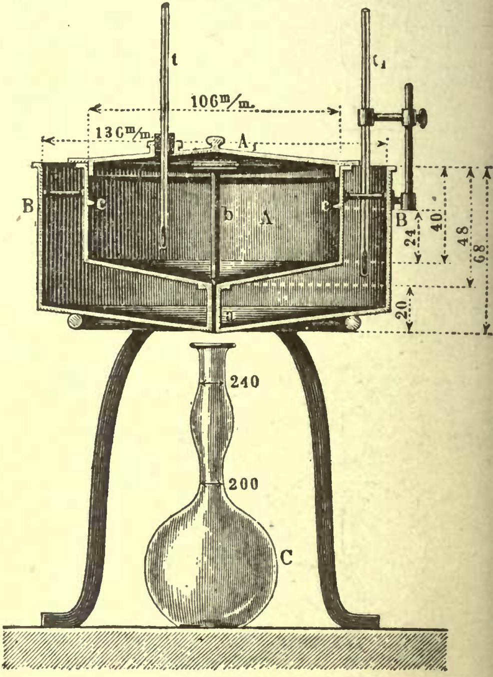

Fig. 28A.

The Mason viscometer was thus described:—

'A glass cylinder 22 ins. (55·9 cm.) long, 1¼ ins. (3·18 cm.) diameter, has a brass lowe head $\frac{1}{8}$ in. (0·318 cm.) thick. An orifice is bored in the centre $\frac{1}{32}$ inch (0·794 cm.) in diameter, with bevelled edges, chamfered back $\frac{1}{2}$ in. (1·27 cm.), thus producing a sharp-edged orifice. A line marking the 18-in. (45·72 cm.) level is cut with several finer lines above and below, $\frac{1}{8}$ in. (0·318 cm.) apart, ranging from 16 to 21 in. (40·64–53·34 cm.) above the orifice. The standard temperature is usually 60°F. (15·5°C.). A total flow of 6·103 cu. in. (100 c.c.) is recorded by adjusting the supply so that the head shall be as nearly as possible equal to 18 ins. (45·72 cm.) of water, determining this head by calculation from the sp.gr. of the oil. The rule for obtaining the viscosity is to note the time required to discharge the 100 c.c. (6·103 cu. ins.) and divide this time by that required where water under a head of 18 ins. (45·72 cm.) is used. This ratio is the measure of the viscosity.'

In the Barbet viscometer the oil under examination is caused to flow through an annular space formed by fixing an iron rod 4 mm. in diameter precisely in the middle of a brass tube 5 mm. in internal diameter. Increased resistance to the flow of the liquid is thus created, and the apparatus is stated to be more sensitive than an ordinary jet viscometer.

Lepenau's 'leptometer' (Fig. 29) consists of two similar metallic cylinders placed vertically side by side in a water-bath, and provided with three pairs of interchangeable jets to be inserted in the stopcocks at the bases of the cylinders. A standard oil having been placed in one cylinder, and the oil to be tested in the other, a pair of jets delivering the oil in drops is selected, and the number of drops falling from the two cylinders between two coincidences of dropping is noted. With dissimilar oils, however, the number of drops is not necessarily a measure of the quantity flowing through the jet, since the size of the drop varies with the nature of the oil.

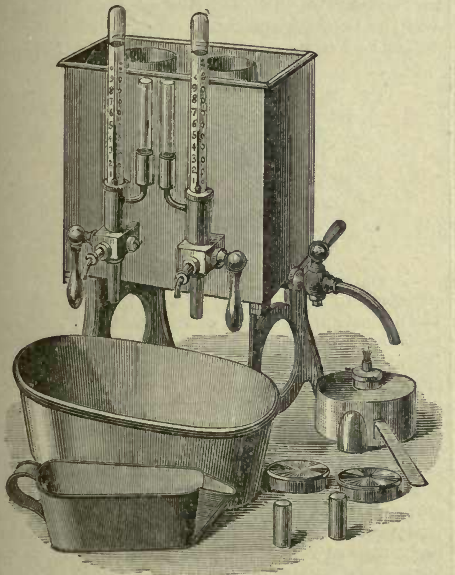

FIG. 29.

McNaught's instrument for testing oils consists of two discs, the lower one provided with a raised edge and attached to a vertical spindle revolving in bearings; the upper one resting on a pivot. The space between the two discs having been filled with the oil to be tested, the lower disc is caused to revolve at a given speed. The upper disc is prevented from partaking of the motion of the lower disc, communicated through the oil, by a projecting pin which comes into contact with a pendulum; the extent to which the pendulum is removed from the perpendicular being the measure of the viscosity of the oil.

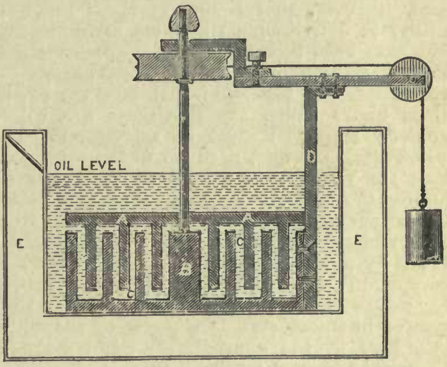

FIG. 30.—Section.

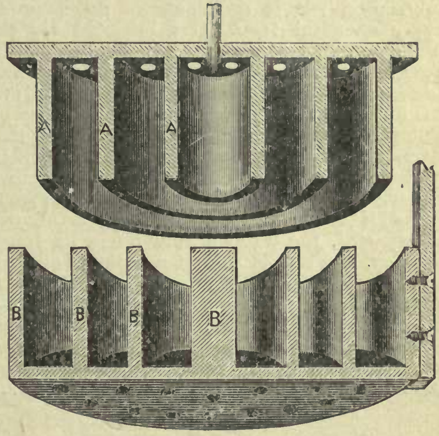

FIG. 31.—Perspective section.

A, A, A. Concentric rings, $\frac{1}{10}$in. thick, $\frac{3}{4}$ in. deep. B, B, B. Ditto. C, C. Spaces of $\frac{1}{10}$ in. between fixed and moving rings. D. Support for driving gear. E, E. Jacket.

The paddle viscometers of Napier of Glasgow and Cockerell of Manchester are based upon the principle of taking the speed of a paddle-wheel revolving in the oil as a measure of the viscosity. A series of concentric rings, on a vertical axis, revolving in concentric annular spaces (Figs. 30 and 31), and a hollow vertical drum revolving in a cylinder of slightly greater diameter containing the oil have also been employed by Napier. The use of a pendulum oscillating in the oil has besides been proposed. Another method of estimating viscosity which has been suggested is to note the length of time occupied in the ascent of a bubble of air through a given column of liquid, and Mills has carried out this idea by using hollow glass bulbs, but without obtaining promising results.

g. Lubricating property by direct mechanical tests. Machines have been devised by Thurston, Woodbury, Ingram and Stapfer, and others, for the mechanical testing of lubricating value. These machines are provided with accurately fitting frictional surfaces, between which the oil to be tested is placed, the heat and resistance at given speeds being determined. It cannot be said, however, that results of much practical utility in determining the value of lubricating oils have thus been obtained. Experience has, in fact, demonstrated that in any machine for the mechanical testing of such oils, the conditions under which the lubricants are to be actually employed must be reproduced. The writer has, therefore, been led to the conclusion that the viscosity of a mineral lubricating oil affords the best guide to its lubricating value, the consumer being thus enabled to select from time to time oils similar to those which he has found by practical experience to afford the best results in the particular circumstances of his case. This branch of the subject has been treated in some detail in a paper by the writer published in the Journal of the Society of Chemical Industry (1886, 5, 121).

h. Purity. In the examination of mineral lubricating oils it is sometimes necessary to apply chemical tests. Oils intended for the lubrication of steam-engine cylinders should be pure hydrocarbons, saponifiable oils being liable to decomposition by the high-pressure steam, and the liberated fatty acids forming metallic soaps. The percentage of saponifiable oils present may be readily determined by treatment with alcoholic potash and extraction of the soap from the aqueous solution with ether. When a mineral lubricating oil is boiled with water and the liquids allowed to separate, the water should retain its transparency, and should exhibit no acid or alkaline reaction. Occasionally mineral lubricating oils are adulterated with resin oil, and their viscosity is increased by the addition of aluminium palmitate or oleate, or of india-rubber. If the presence of any of these adulterants is suspected the oil should be subjected to analytical examination.

6. *Paraffin.*

a. Melting-point. The so-called melting-point of paraffin is understood in the trade to be the temperature at which the melted material begins to solidify. The two methods chiefly adopted in determining this point are known respectively as the English test and the American test. The English test is conducted by melting the paraffin in a test-tube about ¾ in. in diameter, and stirring the fluid material with a thermometer while the tube is held in the air until in the process of cooling a point is reached at which the crystallisation of the hydrocarbons liberates enough heat to arrest the reduction of temperature, and the mercury remains stationary for a short time. Saybolt has devised a convenient form of apparatus for applying this test simultaneously to several samples, the melted material being contained in a series of parallel troughs mounted on a carriage so as to travel backwards and forwards, the thermometers being held rigidly above the troughs in a frame in such a position that the bulbs are just immersed. The American test is made by melting enough of the material to three-parts fill a hemispherical dish about 3¾ ins. in diameter, allowing the paraffin to cool in the air and noting the temperature at which a very thin film extends from the sides of the vessel to a thermometer with a round bulb half an inch in diameter suspended in the middle of the dish so that the bulb is only three-fourths immersed. The melting-point by the American test is usually from 2½°–3°F. higher than that indicated by the English test. Some operators prefer to note the temperature at which a minute quantity of the sample, previously fused into a capillary tube (care being taken not to overheat the material), becomes solidified when the tube is allowed to cool slowly by the side of a sensitive thermometer in a beaker of water.

b. Percentage of oil. The determination of the percentage of oil in paraffin scale is a purely arbitrary test, as there is no natural line of demarkation between the solid and liquid hydrocarbons of petroleum. The test is made by subjecting the material to pressure and noting the loss in weight, but the results obtained depend upon the temperature at which the operation is conducted, the quantity of material in relation to the diameter of the press-cake and the amount and duration of pressure. The writer had some years ago a press (Fig. 32) constructed for the purpose with a steel crosshead, the deflection of which was magnified by levers, and the amount of pressure applied was thus indicated, and he now makes use of a press (Fig. 33) wherein a heavily weighted lever is used to regulate the pressure. Both these presses are provided with circular press-cups and plungers 5⅝ ins. in diameter, and the pressure employed in testing American paraffin scale is 9 tons on the total surface. The quantity of material operated upon is 500 grains, and the pressure is applied for 5 minutes at a temperature of 60°F. The paraffin is placed between circular pieces of calico cut with a steel punch to fit the press-cup, and the oil expressed is absorbed by a sufficient number of discs of blotting-paper placed above and below the cloth containing the cake. The temperature of the press-cup and the plunger is indicated by thermometers inserted in mercury-cups, and the paraffin is also brought to the standard temperature before being pressed. The testing press designed by McCutchon (Figs. 34 and 35) is furnished with a helical steel spring, the extent of compression of which indicates the amount of pressure applied. Messrs. Clarkson and Beckitt, of Glasgow, have made an excellent hydraulic press (Fig. 36) for the

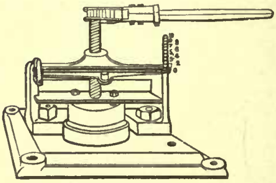

FIG. 32.

purpose, which occupies less space than a lever press.

c. Percentage of water and dirt. The percentage of water in paraffin scale may be determined by heating a weighed quantity in an evaporating dish to a temperature somewhat above the boiling-point of water, the melted paraffin being continuously stirred until the whole of the water has been driven off, when the loss in weight is noted. If the quantity of water present is large the percentage may be determined by distillation or by subsidence, the paraffin being retained in a melted state until the water has separated. Sutherland[1] has introduced a convenient form of apparatus for making the latter test, consisting of a bulbed tube (taking a charge of 50 grams of paraffin) the lower part of which is graduated. In the use of this instrument the greater portion of the melted paraffin may be readily poured off by removing the tube from the heating-bath when the water has separated, and plunging the lower end into cold water so as to seal the water by causing the solidification of a layer of paraffin above it.

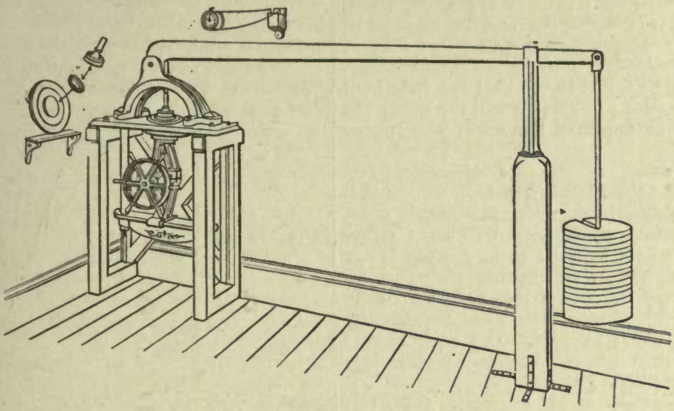
FIG. 33.

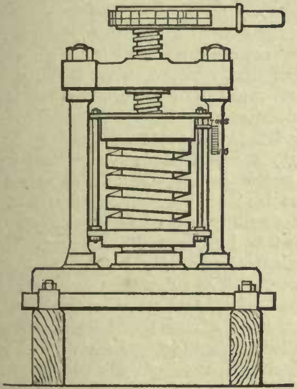
FIG. 34.

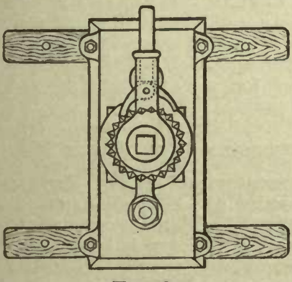
FIG. 35.

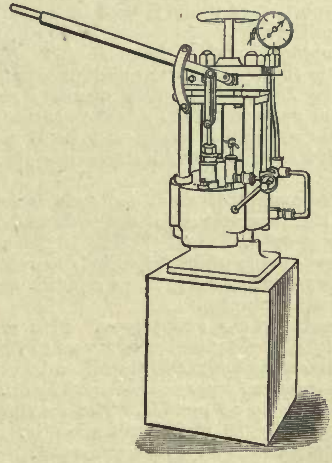
FIG. 36.

The operation may then be completed by dissolving the remaining paraffin in warm petroleum spirit (hydrated). In this method of testing, the dirt is usually estimated with the water, but if the proportion of dirt is considerable it should be collected on a filter paper, washed with mineral spirit, dried and weighed.

The following methods of testing Scotch paraffin scale and heavy mineral oils were agreed upon by the chief chemists of the Scottish Mineral Oil Association, Price's Patent Candle Company, and the writer.

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[1] J. Soc. Chem. Ind., 1887, 6, 123.

I. Scale Analysis.

1. *Sampling of hard scale.* The sample is to be taken by means of a metal tube, which is made slightly conical; the small end is inserted in the scale, and by means of a handle, which is removable, it is forced through the scale to be sampled. By this means a cylindrical core of paraffin is obtained.

Care must be taken to see that the tube is of such a length that the sample will represent the whole length or depth of the cask, waggon, or bing.

2. *Preservation of samples of scale.* Immediately after the sample has been drawn it is to be thoroughly mixed, placed in suitable wide-mouthed bottles, which may be closed either with glass stoppers or good corks; if the latter are used, they should be covered with paraffin paper or soaked in melted paraffin wax before being inserted. The bottles are then finally sealed in the usual manner. The scale should be tightly packed into the bottles, which should be completely filled.

3. *Determination of oil in scale.* (a) *Press to be used.* While no one special form of press is recommended for general adoption, the press used must have some arrangement for indicating the pressure applied. The cup in which the scale is placed during the application of pressure to have an area of 20 sq. ins.

(b) *Preparation of the sample.* A quantity of the scale, after having been freed from water and dirt by melting and subsidence, is to be allowed to cool over night to a temperature of 60°F. The solid mass is then ground to a fine powder, a portion of which is used in the determination of the oil.

(c) *Quantity of scale to be used.* The quantity of scale to be used in the determination of oil is to be 250 grains, which quantity may, however, be reduced to 150 grains in the event of the scale containing much oil (over 7 p.c.). With 'soft' scale the smaller quantity should be taken.

(d) *Temperature at which the scale is to be pressed.* The temperature of the scale and the press is to be 60°F.

(e) *Time during which the scale is to remain under pressure.* The scale is to remain under pressure for 15 minutes.

(f) *Pressing cloths and papers.* Fine linen pressing cloths and a number of layers of filter-paper, sufficient to absorb all the oil, to be used. The exterior papers must not be soiled by oil.

(g) *Pressure to be applied.* The maximum pressure is to be 10 cwt. per square in. and the working pressure 9 cwt. per square in.

4. *Determination of water in scale.* The amount of water present in scale may be determined by either of the following processes:

(a) Distillation from a copper flask. From 1 to 2 lbs. of the scale are heated in a conical copper flask of about the dimensions shown in the annexed sketch; this is connected to an ordinary Liebig condenser. By means of a powerful Bunsen burner or lamp, the water, accompanied by a small quantity of light oil, is volatilised and condensed. The distillate is received in a narrow graduated measure, so that the volume of water can be readily ascertained. As a little water usually adheres to the sides of the condenser tube, this is to be washed out with hydrated gasoline or naphtha and added to the principal quantity.

(b) Price's Company's method. 500 grains of the scale to be tested are weighed in a tared porcelain basin and heated with constant stirring to 230°F. until bubbles cease to be given off; the loss is then determined.

500 grains of the same scale, which has been freed from its water and dirt by melting at a gentle heat and subsidence, are to be heated in the same way, to a similar temperature, and for the same time, and the loss again determined. The loss in the second instance is now to be deducted from the loss found in the first experiment, and the remainder is then to be taken as the quantity of water present.

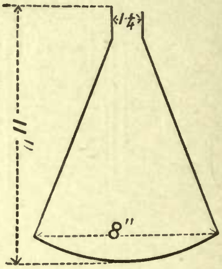


Fig. 37.

5. *Determination of dirt in scale.* The amount of dirt present in scale is to be determined by melting a weighed quantity of the scale and, after subsidence, pouring off the clear paraffin. The residue is then mixed with naphtha, thrown on a weighed dry filter-paper, washed with naphtha or gasoline, dried and weighed. When available, the quantity of scale to be used in the determination of the percentage of dirt should not be less than 7000 grains.

6. *Calculation of the results of the analysis of scale.* As the oil is determined on scale which has been freed from water and dirt, the result must be calculated back to the original scale containing water and dirt.

7. *Determination of the melting (setting) point of solid paraffin.* This is to be determined by what is known as the 'English' test, *i.e.* a test-tube about 1 in. in diameter is filled to the depth of about 2 ins. with the melted paraffin, a small thermometer is inserted, and the whole steadily stirred, while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for a short time is the melting (setting) point.

II. Flashing-point of Heavy Mineral Oil.

8. *Determination of the flashing-point of heavy mineral oil.* The oil cup and cover of the ordinary 'Abel' flash-point apparatus are to be employed. The cup is filled with oil in the usual manner, and the rate of heating is to be such that at least 15 minutes are taken in raising the temperature of the oil to 300°F. In the event, however, of a dispute arising as to the correct flashing-point of a heavy mineral oil, the question is to be decided by means of the 'Pensky-Martens' apparatus (J. Soc. Chem. Ind. 8, 734).

III. VISCOSITY OF MINERAL OIL.

9. *Determination of the viscosity of mineral oil.* The instrument known as the 'Redwood' viscometer is that which is to be employed in the determination of the viscosity of mineral oils. The instrument is to be standardised according to the directions given by Mr. Boverton Redwood (J. Soc. Chem. Ind. 5, 127). Ordinary results are to be expressed, as the time in seconds which 50 c.c. of the oil take to flow through the orifice at a temperature of 70°F.

IV. SETTING-POINT OF MINERAL OIL.

10. *Determination of the setting-point of mineral oil.* This is determined in the following manner. Into a test-tube having a diameter of about 1¼ ins. the oil to be tested is added to the depth of about 2 ins.; the tube is then immersed in a freezing mixture, the oil being slowly stirred with a thermometer until it is cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing mixture, the oil constantly stirred with the thermometer, and the point carefully watched at which the last trace of solid paraffin disappears. This operation is repeated with the same sample of oil until two experiments give concordant results, the temperature so found being the setting-point.

7. *Gas and fuel oils.*

'Gas oils' (mineral oil distillates used in the manufacture of gas for illuminating purposes or for the enrichment of coal-gas) are tested for specific gravity, flash-point, and freedom from water and dirt. In some cases a distillation test designed to secure uniformity in the oils supplied is also carried out.

Oils intended for use as liquid fuel are examined for the presence of water and of solid particles of foreign matter capable of blocking the burners, as well as for specific gravity, flash-point, fluidity at 32°F., calorific value, and percentage of sulphur.

Calorific value. This is best determined by burning one gram in a bomb calorimeter of the Mahler or similar type. Accuracy to within about half of 1 p.c. may be obtained with careful working.[1]

Sulphur. After the determination of the calorific value, the gaseous products of combustion in the bomb are led through a slightly alkaline scrubber, the liquid in which is added to the rinsings of the bomb and the whole precipitated with barium chloride in the usual manner.

B. R.

PE-TUN-TSE, PE-TUN-SE, or **PETUNTZITE** *v.* CHINA-STONE.

PEUCEDANUM (ANETHUM) GRAVEOLENS (Benth. et Hook.). The common Dill, cultivated in England and the South of Europe. Has a hot sweetish taste; is used in medicine and for flavouring spirituous cordials.

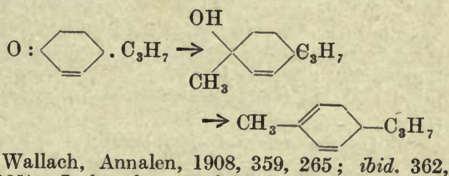
PEWTER *v.* TIN.

PHASEOLUNATIN *v.* GLUCOSIDES.

PHELLANDRENE $C_{10}H_{16}$ is a terpene which occurs in many oils such as that of *Eucalyptus amygdalina* (Labill.) (Baker and Smith, J. Soc. Chem. Ind. 1899, 302; Wallach, Annalen, 1905, 343, 28); in cinnamon oil (Dayk, Chem. Zentr. 1896, ii. 358; Schimmel & Co., *ibid.* 1910, i. 1720); in the oils of schinus molle (Wallach, *ibid.* 1905, ii. 674); of *Juniperus phoenicea* (Linn.) (Rodié, Bull. Soc. chim. 1906, [iii.] 35, 922); of *Abies sibirica* (Ledeb.) (Schindelmeiser, Chem. Zeit. 1907, 31, 759); of the sassafras bark and leaves (Power and Klebber, Chem. Zentr. 1897, ii. 42); in the seeds of *Monodora Grandiflora* (Benth.) (Leimbach, *ibid.* 1909, ii. 1870); in elemi oil (Glover, *ibid.* 1907, i. 1794); in the resins of elemi wood (*Canarium luzonicum* [Miq.]) (Wallach and Rheindorf, Annalen, 1892, 271, 310; Bacon, Chem. Zentr. 1909, ii. 1448); in bitter fennel oil (Cahours, Annalen, 1842, 41, 74; Wallach, *ibid.* 1887, 239, 40; *ibid.* 1904, 336, 10); in water fennel oil (*Oenanthe Phellandrium* (Lam.)) from which the name is derived (Pesci, Gazz. chim. ital. 1886, 16, 225), and in many other oils (*see* Biochemisches Handlexikon, 1910, vii. 295).

It is one of the most unstable of the terpenes, and occurs in two modifications, the α- and β- or *pseudo*, the former of which is usually present in greater quantity than the latter. Neither of these has, however, ever been obtained quite pure (Kondakoff, J. pr. Chem. 1908, [ii.] 78, 42).

α-Phellandrene exists in dextro- and lævo-rotatory modifications. The chief sources of *d*-α-phellandrene are bitter fennel, elemi, and schinus oil. It is also the chief constituent in the dry distillation of certain elemi resins, whilst the chief source of *l*-α-phellandrene is eucalyptus oil (Wallach, Annalen, 1904, 336, 10). The purest natural α-phellandrene so far obtained has b.p. 61°/11 mm., sp.gr. 0·844 at 19° (*d*—α), and b.p. 65°/12 mm., sp.gr. 0·846, at 19° (*l*—α), at ordinary pressure the b.p. is 173°–176°. The optical rotation depends on the source of the phellandrene. α-Phellandrene has been synthesised from *iso*propyl-Δ^2-hexenone by treating the latter with magnesium methyl iodide thus:



(Wallach, Annalen, 1908, 359, 265; *ibid.* 362, 281). It has b.p. 175°–176° (decomp.), sp.gr. 0·841 at 22°.

α-Phellandrene has also been synthesised from Δ^6-menthene-2-one by treating it with phosphorus pentachloride and reducing the product thus obtained with zinc-dust in methyl alcohol solution, or by reducing menthenone-2-oxime with zinc-dust and glacial acetic acid, and distilling the Δ^6-mentheneamine so formed *in vacuô* with phosphoric acid. The α-phellandrene so obtained has b.p. 66°/14 mm., 70°/15 mm., sp.gr. 0·8473 at 21° α_D +45° (Harries and Johnson, Ber. 1905, 38, 1832; *see* also Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193; 1907, [ii.] 75, 141).

α-Phellandrene combines directly with two atoms of bromine forming a dibromide which, when boiled with alcoholic potash, yields cymene (Wallach and Herbig, Annalen, 1895, 287, 371; Bacon, *l.c.*). When treated with alcoholic sulphuric acid α-phellandrene yields terpinene (Wallach, Annalen, 1887, 239, 44; 1889, 252, 102); and when reduced with sodium and amyl alcohol it yields dihydrophellandrene (Δ′-*p*-menthene) $C_{10}H_{18}$, b.p. 171°–172°, α_D +25°, sp.gr. 0·829 (Semmler, Ber. 1903, 36, 1035, 1753; Bacon, *l.c.*). On oxidation with potassium permanganate α-hydroxy-β-*iso*propylglutaric acid $C_3H_{14}O_5$ and its lactone $C_8H_{12}O_4$, are formed; but when it is exposed to atmospheric oxygen *dihydroxyphellandrene* $C_{10}H_{18}O_2$ is produced. The latter crystallises in needles, m.p. 164·5°–165·5° (Clover, Amer. Chem. J. 39, 613).

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[1] A full translation into English of the descriptive pamphlet issued by the makers of the Mahler bomb is included in Hick's Mineral Oil Testing (Griffin).

Phellandrene reacts with halogen acids forming mono- and di-additive compounds. *Phellandrene monohydrochloride* has b.p. 80°–83°/1 mm., and when boiled with excess of alcoholic potash yields *dipentene* (Bacon, *l.c.*; *see* also Wallach, Annalen, 1887, 239, 44; Chem. Zentr. 1902, i. 1293; Kondakoff and Schindelmeiser, *l.c.*; Kondakoff, *ibid.* 1908, 78, 42). The most characteristic compounds of phellandrene are the nitrites or nitrosites $C_{10}H_{16}NO{\cdot}NO_2$. They were first discovered by Cahours, and are prepared by the action of nitrogen oxides on the corresponding phellandrene in ligroin solution or by mixing an equal weight of aqueous sodium nitrite with a solution of the phellandrene in light petroleum and then adding gradually the equivalent quantity of glacial acetic acid. They are purified by solution in acetone and fractional precipitation with water or by dissolving in chloroform and precipitating with methyl alcohol (Cahours, *l.c.*; Wallach and Herbig, Annalen, 1895, 287, 373; Wallach, *ibid.* 1900, 313, 345; 1904, 336, 13; Helbronner, Compt. rend. 1901, 133, 43; Schindelmeiser, Chem. Zeit. 1907, 31, 759).

α-Phellandrene yields two modifications which may probably be regarded as *cis-* and *trans-* forms of the nitrosites:—

α-*Modification* has m.p. 113°–114° (Wallach), 120°–121° (Schreiner, Chem. Zentr. 1901, ii. 544), but according to Clover (*l.c.*) the melting-point depends on the temperature of crystallisation of the nitrosite (*see* also Leimbach, *l.c.*) $[\alpha]_D$ +136°–143° (from *l*-phellandrene), $[\alpha]_D$ −138° (from *d*-phellandrene).

β-*Modification*, m.p. 105°–106° $[\alpha]_D$ −40·8° (from *l*-phellandrene), $[\alpha]_D$ +45·8° (from *d*-phellandrene).

The nitrosites do not react with bromine, and are not readily attacked by potassium permanganate, the products of oxidation being active *iso*propylsuccinic acid, and *iso*butyric acid. When oxidised with nitric acid, the products are trinitrotetrahydrocymene (chiefly) $C_{10}H_{15}N_3O_6$, m.p. 136°–137°, terephthalic, *iso*butyric and *iso*propylsuccinic acids. When reduced with zinc-dust and glacial acetic acid, the nitrosites yield *α-phellandrene diamine* $C_{10}H_{16}(NH_2)_2$, b.p. 251°–254°, 132°–134°/17 mm. (Wallach, Annalen, 1902, 324, 270; *ibid.* 1904, 336, 42; Kondakoff, J. pr. Chem. 1903, [ii.] 68, 294), but when reduced with sodium and alcohol, they yield tetrahydrocarveol, and tetrahydrocarvylamine. The action of hydrochloric and of sulphuric acid and of ammonia on the nitrosites has also been studied (Wallach, Annalen, 1904, 336, 26, 28; *ibid.* 1900, 313, 346).

Nitro-α-phellandrene is obtained by the action of alcoholic potash or acetyl chloride on the nitrosite (Annalen, 1887, 239, 42; 1895, 287, 374; 1904, 336, 31; 1900, 313, 349; Semmler, Ber. 1903, 36, 1754). It is a pale yellow oil with a quinone-like odour, b.p. 134°–138°, 125°–129°/9 mm., and gives with sodium and alcohol the same reduction products as the nitrosite. Its optical rotation is in the same sense as that of the nitrosite employed.

β- or *pseudo-Phellandrene* is obtained chiefly from water-fennel oil, also from schinus oil, and in small quantities from that of *Eucalyptus globulus.* Attempts have been made to obtain it synthetically by treating carvomenthenedibromide with alcoholic potash (Kondakoff and Schindelmeiser, J. pr. Chem. 1905, [ii.] 72, 193), or by treating *iso*propylhexenone with bromacetic ester in presence of zinc; then removing water from the hydroxy ester so formed, and hydrolysing the product (Wallach, Chem. Zentr. 1908, i. 2166). The substances so obtained gave the reaction of β-phellandrene, but could not be obtained pure. It has b.p. 170°–172°, 57°/11 mm., sp.gr. 0·8520 at 20°, $[\alpha]_D$ +18·54. On reduction it yields the same dihydrophellandrene as the α-compound, and, like the latter, it combines with two atoms of bromine, forming a dibromide which, unlike the α-dibromide, reacts with alcoholic potash forming a *monobromoethoxy ether*, b.p. 125°–135°/10 mm. (Semmler, Ber. 1903, 36, 1753). β-Phellandrene reacts with hydrochloric acid, forming pinene hydrochloride and dipentene dihydrochloride (Kondakoff and Schindelmeiser, J. pr. Chem. 1907, [ii.] 75, 141).

When β-phellandrene is oxidised with excess of potassium permanganate, the final product is *iso*butyric acid, but at a low temperature and with excess of the hydrocarbon the following products are obtained, 1-*iso*propyl-Δ^2-cyclohexene-4-one, *iso*butyric acid, α-*iso*propylglutaric acid, and a syrupy *glycol* $C_{10}H_{16}(OH)_2$, b.p. 150°/10 mm., which, on distillation with sulphuric acid in steam, gives tetrahydrocuminaldehyde identical with phellandral (Wallach, Annalen, 1905, 340, 1; *see* also Semmler, Ber. 1903, 36, 1749). When oxidised with free oxygen, β-phellandrene yields 1-*iso*propyl-Δ^2-*cyclo*hexene-4-one, b.p. 103°–106°/15 mm., sp.gr. 0·9387 at 26°, the semi-carbazone of which melts at 183°–184° (Wallach, Annalen, 1905, 343, 30).

β-Phellandrene nitrite or *nitrosite* $C_{10}H_{16}N_2O_3$ exists in two modifications; *α-nitrosite* has m.p. 102° $[\alpha]_D$ −159·3°; β-modification has m.p. 97°–98°, and is almost optically inactive (Wallach, Annalen, 1904, 336, 43; 1905, 340, 1).

The nitrites of β-phellandrene are more readily soluble than those of α-phellandrene. On reduction with sodium and alcohol various basic products and cuminaldehyde (m.p. of semicarbazone, 210°–211°) are formed, whilst if carefully reduced with zinc-dust and acetic acid lævo-rotatory *β-phellandrene diamine*

$$C_{10}H_{16}(NH_2)_2,$$

b.p. 260° (decomp.), 133°–135°/11 mm. is formed (Wallach, Annalen, 1902, 324, 278). This diamine gives a number of distinctive derivatives.

Nitro-β-phellandrene $C_{10}H_{15}NO_2$ is obtained by treating the β-nitrosite with ammonia or potash (Pisci, *l.c.*; Wallach, Annalen, 1904, 336, 44; 1905, 340, 3; *ibid.* 343, 38); on reduction it yields dihydrocuminaldehyde, tetrahydrocuminylamine, cuminylamine, and other basic substances. According to Bacon (*l.c.*), in addition to the α- and β-phellandrenes contained in elemi wood resins, there is another phellandrene having b.p. 175°–178°, sp.gr. 0·8375, at 30°/4° $[\alpha]_D^{30°}$ 82·4.

Phellandral (*tetrahydrocuminaldehyde*) (*v. supra*) $C_{10}H_{16}O$ has been obtained from *Phellandrium aquaticum* after removal of the phellandrene. It is isomeric with citral, and boils at 220°–230°, 89°/5 mm., sp.gr. 0·9445 at 15°, $\alpha_D - 36°\ 30'$. It gives a semi-carbazone, m.p. 204°, an oxime, m.p. 87°–88°, and a phenylhydrazone, m.p. 122°–123°. On exposure to the air it forms the crystalline acid $C_{10}H_{16}O_2$, and when oxidised with potassium permanganate it yields the dibasic acid $C_9H_{16}O_4$ (J. Soc. Chem. Ind. 1904, 1236).

PHENACETIN *p-acetphenetidine*

$$C_2H_5O{\cdot}C_6H_4{\cdot}NH{\cdot}COCH_3$$

is prepared by ethylating *p*-nitrophenol by Kolbe's method (J. pr. Chem. [ii.] 27, 424), reducing the nitrophenetole and acetylating the resulting aminophenetole by boiling with glacial acetic acid (Platt, J. Anal. and Appl. Ch. 1893, 77; Hinsberg, Annalen, 1899, 305, 278; Täuber, D. R. P. 85988).

According to Paul (Zeitsch. angew. Chem. 1896, 587) phenacetin is prepared by heating a mixture of 16·7 grams of *p*-aminophenetole hydrochloride, 8·7 grams of sodium acetate, and 83 grams of acetic acid under a reflux condenser for 3 hours. The mixture is then poured into ten times its volume of boiling water and the solution is filtered. On cooling, phenacetin separates out, and can be purified by repeated recrystallisations. The yield is 90 p.c. of the theoretical.

It crystallises in colourless needles, melts at 135°, and is sparingly soluble in water, soluble in glycerol, and readily soluble in alcohol or acetic acid (Hinsberg and Kast, Chem. Zentr. 1887, 358; Utescher, J. Soc. Chem. Ind. 1888, 87; Seidell, Amer. Chem. J. 1907, 1088). According to Dujardin-Beaumetz (Chem. and Drug. 33, 244), phenacetin, if toxic, is only so in slight degree. It is a safe and trustworthy antipyretic, entirely free from injurious secondary effects, and in doses of 0·2–0·5 gram produces a gradual lowering of temperature during 4–6 hours, when a maximum depression of 2° is reached, D.-B.; H. and K.; U.; Ghillany, J. Soc. Chem. Ind. 1887, 676; Kobler, Chem. Zentr. 1887, 1092; Hoppe, *ibid.* 1888, 609; Rumpf, *ibid.* 1888, 1103. In larger doses (1–2 grams) it acts as an anti-neuralgic.

Pure phenacetin should answer to the following tests (Platt, *l.c.*):—

(1) When boiled with hydrochloric acid, the filtrate of the cold diluted solution produces a ruby-red colour on the addition of 2 or 3 drops of potassium dichromate.

(2) After boiling with water, the cooled filtered solution should remain clear on the addition of bromine water.

(3) Boiled with hydrochloric acid and ferric chloride, a red colour is produced.

(4) Boiled with caustic potash, alcohol is produced.

(5) Heated with alcohol and sulphuric acid, ethyl acetate is produced.

(6) Sodium persulphate produces a yellow colour when warmed with phenacetin, and this deepens to orange on boiling.

(7) Bromine water when heated with phenacetin solution gives a rose-colour.

(8) With Millon's reagent phenacetin gives a yellow colour passing to red, nitrous fumes are also given off and a yellow precipitate separates (Barral, J. Pharm. Chim. 1904, 237).

(9) When boiled with phosphoric acid of sp.gr. 1·7 a rose colour is produced, passing through red, violet-bluish-green to a dirty green (Raikow and Schtarbanow, Chem. Zentr. 1900, i. 999).

Phenacetin may contain as impurities or adulterations, acetanilide, antipyrine, quinine, exalgin, and other substances (Mannich, B. Pharm. 1906, 57). It also occurs as an impurity in antipyrine and other pharmaceutical substances. Acetanilide may be distinguished by the following methods.

0·1 gram of the sample is boiled with 3 c.c. of a 50 p.c. sodium hydroxide solution, then cooled and shaken with 5 c.c. of sodium hypochlorite solution. If acetanilide be present a purple- or brownish-red turbidity is produced, but if the sample be pure, a clear yellow liquid is obtained (Beringer, Chem. and Drug. 1903, 377).

0·5 gram is boiled with 6 c.c. of water, cooled, filtered, and the filtrate boiled with dilute nitric acid and potassium nitrite. Then a drop or two of Plugge's phenol test is added, and the solution boiled. The appearance of a red colour indicates acetanilide; 2 p.c. of the latter can thus be detected (Schroeder, Arch. Pharm. [iii.] 27, 226). 0·5 p.c. acetanilide can be detected by boiling a gram of the sample with 15 c.c. of water, the solution is then cooled and filtered. On addition of bromine water, a turbidity is produced if the impurity is present owing to the separation of *p*-bromacetanilide (Guasti, L'Orosi, 17, 111).

To detect phenacetin, exalgin, and acetanilide in a mixture, 1 gram of the mixture is treated with 2 c.c. chloroform, which dissolves the exalgin. In aqueous solution antifebrin gives with bromine water a crystalline bromine compound, whereas the other two substances do not give this (Hirschsohn, Pharm. J. 20, 710). Or 2–4 c.c. of the solution is boiled with potash in a test-tube fitted with a rubber cork and bent tube leading into a tube containing 1–3 c.c. of bleaching powder. If acetanilide is present the first few drops produce a violet colour. Exalgin gives a green, turning to a greyish-green colour; if antipyrine is present a yellowish-green colour is produced, whilst if none of these impurities is present, at first the solution remains colourless, then a vermillion-red turbidity is produced, and finally a red substance separates on the surface of the liquid, which itself remains clear yellow (Raikow and Schtarbanow, *l.c.*).

The presence of quinine can be detected by the addition of chlorine water and ammonia when, if quinine is present, a light blue colour will be produced, whereas if the sample is pure the colour is violet-yellow (Sestini and Campani, L'Orosi, 14, 304); or the solution is agitated with bromine vapour and ammonia added drop by drop, the solution turns green, and on being shaken with ether, two layers are formed; the upper is green, indicating quinine, the lower is violet-yellow, and consists of the phenacetin compound (Chem. Zeit. 1892, 368). For other methods and for the detection of other impurities *cf.* Raikow and Schtarbanow, *l.c.*; Luttke, J. Soc. Chem. Ind. 1890, 544; Reuter, Pharm. Zeit. 1891, 185; Goldmann, *ibid.* 208; Platt, *l.c.*; Hyde, Amer. Chem. J. 1895, 933; Schoepp, Pharm. Zeit. 1897, 106; Maas, Chem. Zentr. 1900, ii. 1215. For the estimation of phenacetin *cf.* Turner and Vanderkleed, Pharm. J. 1907, 521.

When finely-powdered phenacetin is boiled with nitric acid, the solution on cooling deposits silky yellow needles of nitrophenacetin

$$OEtC_6H_3(NO_2)NHAc,$$

m.p. 103°. This reaction can serve as a test for distinguishing phenacetin from acetanilide and antipyrine (Autenrieth and Hinsberg, Arch. Pharm. 229, 456). From the nitro-compound *luteol* (*o*-chloro-*m*-hydroxydiphenylquinoxaline), a very sensitive indicator can be prepared (Autenrieth, Chem. Zeit. 1900, 453; Meyer, J. Soc. Chem. Ind. 1909, 328).

With concentrated sulphuric acid phenacetin gives the sulphonic derivative, other compounds being obtained when the strength of the acid is varied (Cohn, Annalen, 1899, 309, 233).

Alkylated phenacetins are obtained by treating a solution of phenacetin in xylene solution with sodium and then acting upon the sodium salt thus obtained with the alkyl halide (Willcox, J. Soc. Chem. Ind. 1891, 384); or by treating the acetyl compound of phenacetin with the corresponding alcohol (Willcox, *l.c.* 854).

The *methyl* compound $EtO{\cdot}C_6H_4NMeAc$, m.p. 40°, has more powerful narcotic properties than phenacetin itself, and the *ethyl* compound, m.p. 38°, still more so. The *iso-propyl* and higher alkyl compounds are less powerful narcotics (Hinsberg, Annalen, 1899, 305, 276).

Penacylphenacetin $OEtC_6H_4NAc{\cdot}CH_2COPh$, m.p. 87°, has been prepared in a similar way, and is a non-poisonous hypnotic antipyretic (Goldschmidt, Chem. Zeit. 1901, 628).

By boiling phenacetin (1 mol.) with acetic anhydride (3–4 mols.) a diacetyl derivative is formed, m.p. 53·5°–54°, which has similar physiological properties to phenacetin, its action being more intense but less lasting than the latter (Bistrzycki and Ulffers, Ber. 31, 2788).

Phenacetin has been chlorinated (Reverdin and Düring, Ber. 1899, 32, 152), and brominated (Hinsberg, *l.c.*; Staedel, Annalen, 1883, 217, 73; Vaubel, Ber. 1899, 32, 1875; J. pr. Chem. 1897, [ii.] 217; Hodurek, Ber. 1897, 30, 477).

By the action of chloracetylchloride on *p*-phentidine the chlorine derivative

$$OEt{\cdot}C_6H_4NHCOCH_2Cl,$$

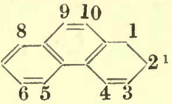
m.p. 145°–146°, is obtained (Bistrzycki and Ulffers, *l.c.*).

When a solution of phenacetin in water, alcohol, or glacial acetic acid is treated with a solution of iodine in potassium iodide, a chocolate-coloured crystalline powder of *iodophenin* $C_{20}H_{25}N_2O_4I_3$ is precipitated, which is applicable to therapeutic purposes (Riedel, J. Soc. Chem. Ind. 1892, 633; D. R. P. 58409) (*v.* SYNTHETIC DRUGS).

PHENACITE *v.* GLUCINUM.

PHENANTHRAQUINONE *v.* PHENANTHRENE.

PHENANTHRENE. 2:2′-*Diphenylene-ethylene*



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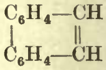

$$\begin{array}{ccc} C_6H_4 & — & CH \\ | & & \| \\ C_6H_4 & — & CH \end{array}$$

Phenanthrene, which was isolated from coal-tar almost simultaneously by Fittig and Ostermayer (Ber. 1872, 5, 933; Annalen, 1873, 166, 361), and by Graebe and Glaser (Ber. 1872, 5, 861, 968, 982; Annalen, 1873, 167, 131; *cf.* Limpricht, Ber. 1873, 6, 532; Hayduck, Annalen, 1873, 167, 177), is the chief constituent of the solid, readily soluble portions of crude anthracene. It constituted about 45 p.c. of the Stuppfett obtained as a by-product in the distillation of Idrian quicksilver ores, but the process is now obsolete.

Formation.—Phenanthrene is obtained with other hydrocarbons when vapours of toluene (Graebe, Ber. 1874, 7, 48), stilbene, dibenzyl (Graebe, Annalen, 1873, 167, 157; Barbier, Ann. Chim. Phys. 1876, [v.] 7, 532), turpentine (Schultz, Ber. 1877, 10, 113), or Baku petroleum residues (Letny, *ibid.* 1878, 11, 1211), or mixtures of diphenyl and ethylene, benzene and styrene, benzene and ethylene (Barbier, *l.c.*), or cumarone and benzene (Kraemer and Spilker, Ber. 1890, 23, 85) are passed through a red-hot tube. It is also present in the product obtained when morphine or codeïne (Vongerichten and Schrötter, Annalen, 1881, 210, 396; Ber. 1882, 15, 1484, 2179), or morphenol (Vongerichten, Ber. 1898, 31, 3202) is distilled with zinc dust.

Preparation.—For the isolation of phenanthrene that portion of crude anthracene which is readily soluble in light petroleum is used. To ensure freedom from phenols of high boiling point it is extracted with caustic soda solution, acridine being removed afterwards with sulphuric acid. The residue is then distilled fractionally, and the fraction boiling at 320°–350° is refractionated between 339° and 342° (G. A. Schmidt, Ber. 1879, 12, 1159). The product, which still contains some anthracene and other hydrocarbon impurities, is crystallised from a large bulk of alcohol to remove these less soluble constituents, phenanthrene being separated from the mother liquor by concentration, and purified by recrystallisation. Wense (Ber. 1886, 19, 761, footnote) recommends the use of toluene as a solvent for the removal of the less soluble anthracene.

Purification can be effected by oxidising the impure material with sufficient potassium dichromate and dilute sulphuric acid (Anschütz and Schultz, Annalen, 1879, 196, 35), to convert anthracene present into the quinone. For this reason crude anthraquinone, produced from crude anthracene, serves as a convenient source of phenanthrene as this hydrocarbon can be extracted from it readily by 85 p.c. alcohol (*cf.* G. A. Schmidt, J. pr. Chem. 1874, [ii.] 9, 256).

Another method of purifying the phenanthrene fraction has been proposed, in which, after removal of acid and basic constituents, the residue is freed from fluorene and diphenylene oxide by fusion with caustic potash at 300°, followed by extraction with hot water. The residue is then distilled to obtain the pure hydrocarbon (Akt. Teer- u. Erd-Oel Ind. D. R.-P. 130679; Eng. Pat. 5047 of 1901; *cf.* Kraemer and Weissgerber, Ber. 1901, 34, 1665).

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[1] Knorr has proposed that 4:5-derivatives should be called *meso*-diderivatives of phenanthrene (Ber. 1903, 36, 3078); also that the numbering of positions in the middle ring should be continued from 10 to 14 (Ber. 1907, 40, 3341).

On the laboratory scale, phenanthrene is purified conveniently by conversion in alcoholic solution into the *picrate*, which crystallises in golden-yellow needles, m.p. 143°–145°, and on treatment with ammonia yields the pure hydrocarbon (Limpricht, Ber. 1873, 6, 532).

Properties.—Phenanthrene crystallises in colourless scales, m.p. 100°, b.p. 340°. It is insoluble in water, but readily soluble in hot alcohol, ether, carbon disulphide, acetic acid, or benzene, showing blue fluorescence in solution. 100 parts of toluene dissolve 33·02 parts at 16·5°; 100 parts of absolute alcohol dissolve 2·62 parts at 16°; or 10·08 parts at 78° (Bechi, Ber. 1879, 12, 1978); and 100 parts of 95 p.c. alcohol dissolve about 2 parts at 13°–14° (Graebe, Annalen, 1873, 167, 136).

Reactions.—(1) Oxidising agents convert phenanthrene into *phenanthraquinone*, or by further oxidation into *diphenic acid* (Fittig and Ostermayer, *l.c.*), but with a large excess of 100 p.c. sulphuric acid and some mercury at 300° *phthalic acid* is obtained (Bad. Anilin- u. Soda-Fab. D. R.-P. 91202; Eng. Pat. 18221 of 1906).

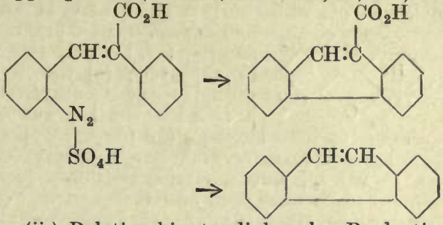
(2) Chlorination in presence of halogen carriers leads to the production of 9 : 10-*dichlorophenanthrene*, needles, m.p. 160°–161° (J. Schmidt and Ladner, Ber. 1904, 37, 4403), and of 2 : 9 : 10-*trichlorophenanthrene*, needles, m.p. 123°–124° (Schmidt and Schall, *ibid.* 1906, 39, 3892).

(3) With bromine in the cold it forms the *dibromide*, prisms, m.p. 98°, which, heated at its melting point, or with water, decomposes into 9 (10)-*bromophenanthrene*, prisms, m.p. 63° (Fittig and Ostermayer, Annalen, 1873, 166, 363; Hayduck, *l.c.*; Zetter,[1] Ber. 1878, 11, 165; Austin, Chem. Soc. Trans. 1908, 93, 1763). Bromination in boiling chloroform solution leads to the formation of 3 : 9- (or 10)-dibromophenanthrene, needles. m.p. 146° (Schmidt and Ladner, Ber. 1904, 37, 3577) from phenanthrene, but of 2 : 7-*dibromophenanthrene*, needles, m.p. 199°–200°, from α-tetrahydrophenanthrene (Schmidt and Mezger, *ibid.* 1907, 40, 4562).

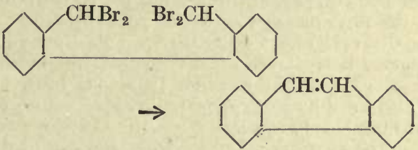
(4) By nitric acid, it is converted into nitro derivatives like naphthalene and not oxidised to quinone like anthracene.

Constitution and syntheses.—The structural formula assigned to phenanthrene at the head of this article was adopted originally to exhibit the relationship existing between the hydrocarbon and diphenic acid, its oxidation product (Fittig and Ostermayer, *l.c.*; Schultz, Annalen, 1879, 196, 1; 1880, 203, 95), or phthalic acid (*cf.* Anschütz and Japp, Ber. 1878, 11, 211). It has been confirmed by several syntheses, from among which three may be selected for reference as establishing the presence of specific radicles or linkings:—

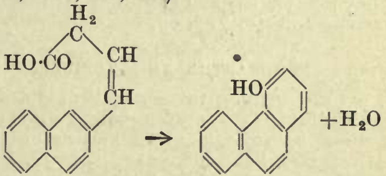
(i.) Relationship to ethylene: Production of phenanthrene by distilling phenanthrene-9-carboxylic acid obtained by the interaction of diazotised α-phenyl-*o*-aminocinnamic acid and copper powder (Pschorr, Ber. 1896, 29, 496).



(ii.) Relationship to diphenyl: Production of phenanthrene by debrominating ωωω′ω′-tetrabromo-2 : 2′-ditolyl by means of sodium (Kenner and Turner, Chem. Soc. Trans. 1911, 99, 2112).



(iii.) Relationship to naphthalene: Production of 4-hydroxyphenanthrene by heating β-naphthyl*iso*crotonic acid, prepared from β-naphthaldehyde by the Perkin reaction (Ludewig, Annalen, 1911, 379, 351).[1]



Pschorr's method has proved to be of wide application in the synthesis of phenanthrene derivatives of known constitution from substituted α-phenyl-*o*-aminocinnamic acids, and, coupled with the investigations of Vongerichten and of Knorr, has made it possible for the relationship between phenanthrene and the morphine group of opium alkaloids to be elucidated.

Chemical activity in the phenanthrene molecule is manifested chiefly at the ethylenic double linking, shown between carbon atoms numbered 9 and 10 in the formula at the head of this article. Here the addition of hydrogen and bromine takes place, here oxidation leading to the production of phenanthraquinone occurs, and here disruption of the molecule follows when more powerful oxidising agents are used—as in the formation of diphenic acid. For the purpose of determining orientation in the phenanthrene molecule, oxidation to diphenic acid is important, as—when substituents occur in positions other than 9 or 10 or 9 and 10—they are found in corresponding positions in the resulting diphenic acids.

Phenanthrene has little value in technical chemistry, but its relationship to some of the alkaloids of opium and of *Corydalis* is of much interest. These alkaloids are methoxy or hydroxy derivatives of tetra- or hexa-hydrophenanthrene, the parent substance associated with the nitrogen complex in the case of the opium alkaloids being 3 : 6-dihydroxy-4 : 5-phenanthrylene oxide, in the molecule of which (*a*) rings I and II are hydrogenated in morphine and codeïne, but only ring I in thebaïne; (*b*) the hydroxyl radicle is methylated in ring I in codeïne, but in both rings in thebaïne. Of the *Corydalis* alkaloids bulbocapnine, corytuberine, and corydine less is known, but a relationship has been established between their structure, and that of *apo*morphine (Gadamer, Arch. Pharm. 1911, 249, 503; *cf.* Dobbie and Lauder, Chem. Soc. Trans. 1902, 81, 145).

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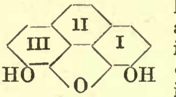
[1] Zetter, also, has described two dibromophenanthrenes, but one of them—the β-compound—is now known to be β-dibromofluorene (Werner and Egger, Ber. 1904, 37, 3027).

[1] Although phenanthrene can be synthesised from naphthalene, the reverse operation has not been accomplished, the lateral rings remaining intact until the middle ring has been broken down by oxidising agents.



The connection between the opium alkaloids and hydroxyphenanthrenes has led to the study of the physiological action of phenanthrene and its derivatives. Phenanthrene and its hydrogenated derivatives are harmless (Hildebrandt, Arch. exp. Path. Pharm. 1908, 59, 140), but 2-, 3-, or 9-hydroxyphenanthrene administered subcutaneously gives rise to acute tetanic symptoms, observed also with certain of the carboxylic and sulphonic acids (Bergell and Pschorr, Zeitsch. physiol. Chem. 1903, 38, 16). There is no evidence to show that phenanthrene derivatives from the molecules of which a quinoline or *iso*quinoline ring is absent can exercise a narcotic action.

PHENANTHRENE HYDRIDES.

9 : 10-*Dihydrophenanthrene* is obtained when phenanthrene is reduced in boiling amyl alcohol solution by sodium, or in presence of finely-divided nickel at 200° by hydrogen (J. Schmidt and Mezger, Ber. 1907, 40, 4240), or in presence of nickel oxide by hydrogen at 320° under 100 atmos. (Ipatiew, Jakowiew and Rakitkin, Ber. 1908, 41, 999). It forms leaflets from alcohol, m.p. 94°–95°, b.p. 312°–314° under 739 mm., and does not react with bromine. The *picrate* forms scarlet needles, m.p. 135°–137° (J. Schmidt and Mezger, *l.c.*).

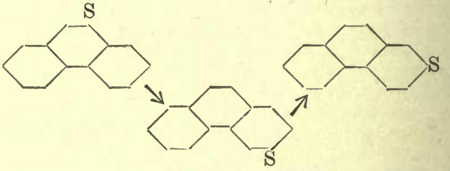
By further reduction with these agents *α*- and *β-tetrahydro-*,[1] and *hexahydro-*, *octohydro-*, *decahydro-*, and *dodecahydro-phenanthrenes* have been obtained. These compounds are oils, the boiling-point and density of which fall as the amount of hydrogen in the molecule is increased. With the exception of the *α*-tetrahydro derivative they do not form picrates (J. Schmidt and Mezger, *l.c.*).

PHENANTHRENESULPHONIC ACID.

Monosulphonation has been effected by the interaction of phenanthrene with an equal weight of sulphuric acid at 100° (Graebe, Annalen, 1873, 167, 152; Schultz and Japp, Ber. 1877, 10, 1661; Japp, Trans. Chem. Soc. 1880, 37, 83); with two-thirds of this weight at 170° [2] (Morton and Geyer, J. Amer. Chem. Soc. 1880, 2, 203); with an equal weight of sulphuric acid at different temperatures between 80° and 165° (Werner, Annalen, 1902, 321, 257); and with chlorosulphonic acid (Pschorr, Ber. 1901, 34, 4004). Disulphonation has been found to occur when phenanthrene is heated with anhydrosulphuric acid at 100° (Fischer, Ber. 1880, 13, 314).

Three monosulphonic acids have been shown to occur in the products obtained by the aid of sulphuric acid. The first of these was isolated by Graebe, and converted by Schultz and Japp into a carboxylic acid, oxidisable to phenanthraquinonecarboxylic acid; it is the [*α*-] or 3-acid, as it yields 3-hydroxyphenanthrene on fusion with caustic potash. The second was isolated by Japp, and by him oxidised to phenanthraquinone: it is the [*β*-] or 9(10)-acid. The third is the 2-acid discovered by Werner and Rekner (Werner, *l.c.*), which gives 2-hydroxyphenanthrene on fusion with caustic potash. With chlorosulphonic acid the product is a mixture of the 2- and 3-sulphonic acids.

The conditions under which these acids are obtained by means of sulphuric acid is shown in the scheme, which allows a comparison to be made with the course of sulphonation in the naphthalene series:



Best yield at 95°–100°; not detected above 130°.

Best yield at 120°–130°; very little above 180°.

Good yield at 120°–130°.

For the separation of the isomerides fractional crystallisation of the lead, barium, calcium, or potassium salts is employed, the solubility in water in each case increasing from the 9(10)- to the 2-acid (Werner, *l.c.*).

Phenanthrene-2-sulphonic acid has not been crystallised. The *lead* salt, $PbA_2,2H_2O$, is crystalline; the *potassium* salt, KA, and *ammonium* salt, NH_4A, form leaflets; and the *methyl ester* scales, m.p. 96°–98°, which show blue fluorescence (Werner, *l.c.*; Pschorr, *l.c.*).

Phenanthrene-3-sulphonic acid forms scales, $HA,2H_2O$, m.p. 88°–89°, HA,H_2O, m.p. 120°–121°; HA, m.p. 175°–177° (Sandqvist, Annalen, 1909, 369, 106). The *lead* salt, $PbA_2,3H_2O$, crystalline granules; *copper* salt, $CuA_2,4H_2O$, scales; *ferrous* salt, $FeA_2,5H_2O$, and *zinc* salt, $ZnA_2,4H_2O$, crystalline powders; *barium* salt, $BaA_2,3H_2O$, scales; *calcium* salt, $CaA_2,2H_2O$, crystalline granules; *magnesium* salt, $MgA_2,4H_2O$, scales; *potassium* salt, KA, scales; *ammonium* salt, NH_4A, scales, have been described (Sandqvist, *l.c.*). The *sulphonyl chloride* crystallises in rhombic prisms, m.p. 110°–111°, also 114°; the *amide* in scales, m.p. 190°; the *methyl ester* in scales, m.p. 119°; and the *ethyl ester* in needles, m.p. 108°.

Phenanthrene-9 (10)-sulphonic acid forms needles; the *barium* salt, $BaA_2,2\frac{1}{2}H_2O$, needles; the *potassium* salt, KA, needles; the *sulphonyl chloride* needles, m.p. 125·5°; and the *anilide* prisms, m.p. 165° (Werner, *l.c.*). For other salts, *cf.* Sandqvist, Annalen, 1912, 392, 76.

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[1] These tetrahydrophenanthrenes are probably the 2 : 7 : 9 : 10- and 4 : 5 : 9 : 10- derivatives, but it is not known which of them has the former, and which the latter constitution.

[2] The "*β*-acid" obtained in addition to Graebe's acid by these authors is not identical with Japp's *β*-acid, and appears to have been 3-acid mixed with some impurity, probably 2-acid (*cf.* Werner, *l.c.*).

NITROPHENANTHRENES.

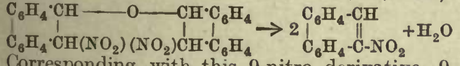
Of the five nitrophenanthrenes the 1-isomeride has not yet been prepared (J. Schmidt and Heinle, Ber. 1911, 44, 1490).

Earlier work on the nitration of phenanthrene with a large excess of fuming nitric acid led to the isolation of three compounds, termed α- (m.p. 73°–75°), β- (m.p. 126°–127°), and γ- (m.p. 170°–171°) nitrophenanthrenes (G. A. Schmidt, Ber. 1879, 12, 1153). It has been shown that of these compounds the α- and γ- are identical respectively with 4- and 3-nitrophenanthrenes, but that the β-compound is a nitro derivative not of phenanthrene, but of fluorene, which accompanies this hydrocarbon in coal-tar (J. Schmidt and Heinle, *l.c.*).

For the production of *nitrophenanthrenes* J. Schmidt has employed two methods. In one, nitration is effected by nitric acid (sp.gr. 1·45) in presence of a mixture of acetic acid and acetic anhydride, leading to the formation of the four isomerides. A summary of the properties and yields of these substances, as recorded by J. Schmidt and Heinle, is given in the table—

NO_2	Yield (approx.)	Crystallisation from alcohol	M.p.	Picrate
2-	20 p.c.	pale yellow rosettes	99°	none
3-[1]	2 p.c.	deep yellow needles	170°–171°	none
4-	20 p.c.	reddish yellow needles	80°–82°	none
9-	60 p.c.	orange yellow needles	116°–117°	98°–99°

In the second method use is made of one of the two additive compounds which phenanthrene, dissolved in benzene, forms with the nitrous gas obtained by the interaction of nitric acid and arsenious oxide. This substance, *nitrodihydrophenanthrene oxide* (m.p. 154°–155°), is converted by sodium methoxide into 9-nitrophenanthrene (J. Schmidt, Ber. 1910, 33, 3257):



$$\begin{matrix} C_6H_4\cdot CH & —O— & CH\cdot C_6H_4 \\ | & & | \quad | \\ C_6H_4\cdot CH(NO_2) & & (NO_2)CH\cdot C_6H_4 \end{matrix} \longrightarrow 2 \begin{matrix} C_6H_4\text{-}CH \\ | \qquad \Vert \\ C_6H_4\text{-}C\text{-}NO_2 \end{matrix} + H_2O$$

Corresponding with this 9-nitro derivative, 9-*nitro*-9 : 10-*dihydrophenanthrene*, a yellow crystalline compound, decomposing at 100°, is obtained on mixing phenanthrene in dry powder with the liquefied nitrous gas (J. Schmidt, D. R.-P. 129990 of 1901).

AMINOPHENANTHRENES.

Four aminophenanthrenes (phenanthrylamines) are known corresponding in orientation with the nitrophenanthrenes. Three methods have been used for their preparation:—

(i.) Reduction of the nitro compound by alcoholic ammonium sulphide (G. A. Schmidt, Ber. 1879, 12, 1156), or stannous chloride and hydrochloric acid (J. Schmidt and Strobel, *ibid.* 1901, 34, 1464), or zinc dust and alcoholic ammonia (J. Schmidt and Heinle, *ibid.* 1911, 44, 1498).

(ii.) Heating the hydroxy compound at temperatures above 200° with ammonia (Japp and Findlay, Chem. Soc. Trans. 1897, 71, 1123; Pschorr and Schröter, Ber. 1902, 35, 2728), or ammonio-calcium chloride, or—for the acetyl compound—ammonium chloride, sodium acetate, and acetic acid (Werner and Kunz, Ber. 1901, 34, 2525).

(iii.) Conversion of the carboxylic acid successively into the hydrazide, azide, and urethane, which is then heated with ammonia (Pschorr and Schröter, *l.c.*; Pschorr, Einbeck, and Spangenberg, Ber. 1907, 40, 2000).

The crystalline character and m.p. of each base and the m.p. of its acetyl and benzoyl derivatives are given in the table—

—	Base	Acetyl	Benzoyl
2-	crystals, 85°	225°–226°	—
3-α-	leaflets, 143°	200°–201°β	213°–214°β
β-	leaflets, 87·5°		
4-	needles, 105°	190°	224°
9-α-	needles, 138°	207°–208°α	190°α
β-	crystals, 104°		

As shown in the table, 3-aminophenanthrene (Werner and Kunz, *l.c.*; Werner, Annalen, 1902, 321, 312; *cf.* J. Schmidt and Sauer, Ber. 1911, 44, 3247) and 9-aminophenanthrene (J. Schmidt and Heinle, *l.c.*) exist in two forms—one stable, the other labile and convertible into it by being heated or kept for some time or acetylated. Both forms of each compound give the same acetyl or benzoyl derivative, from which by hydrolysis the stable form of the base (indicated by the Greek letter) is obtained. The nature of the isomerism has not been established, but it has been attributed to rearrangement of the linkings in the phenanthrene molecule in view of the fact that the two forms of the 9-isomeride have the same molecular weight (J. Schmidt and Heinle, *l.c.*).

Diazotisation of β-3-aminophenanthrene (J. Schmidt, Ber. 1901, 34, 3534; *cf.* Werner and Kunz, *l.c.*), and of 9-aminophenanthrene[1] (J. Schmidt and Strobel, Ber. 1903, 36, 2517) has been effected—in the latter case with the accompanying production of azoxy and azo compounds. But difficulty has been experienced in diazotising 2-aminophenanthrene (Werner and Kunz, *l.c.*), although 2-amino- (like 8-amino-) phenanthrene-9-carboxylic acid forms a diazo compound apparently with ease (Pschorr, Ber. 1906, 39, 3121).

The oxime and dioxime of phenanthraquinone, on reduction with stannous chloride, yield 9 : 10-*aminohydroxyphenanthrene* (Vahlen's 'morphigenine,' *cf.* D. P. Anm. V. 3840 of 1902; Ber. 1902, 35, 3044) and 9 : 10-*diaminophenanthrene* respectively (Pschorr and Schröter, *ibid.* 3733). The former, when heated with water or dilute acid, is converted into 9-*aminophenanthrene* (Schmidt, D. R.-P. 141422 of 1902).

HYDROXYPHENANTHRENES.

The hydroxy derivatives of phenanthrene (phenanthrols) have been investigated largely as a consequence of the relationship which has been established between them, and certain of the opium and *Corydalis* alkaloids. In many cases the constitution of the hydroxyphenanthrenes has been determined by Pschorr's synthetical method, which has shown itself to be of the first importance in the study of the degradation products of these alkaloids. In others, the constitution assigned depends on that of the sulphonic acids, from which some of the hydroxy derivatives have been obtained by fusion with caustic alkali (*cf.* Werner, Annalen, 1902, 321, 276). The constitution, crystalline character, and melting-point of the hydroxyphenanthrenes and of their ethers are given in the table :—

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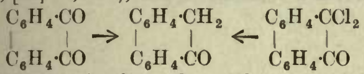
[1] 3-Nitrophenanthrene is obtained in better yield by nitrating phenanthrene with nitric acid of sp.gr. 1·56 at 0° (J. Schmidt and Heinle, *l.c.*).

[1] The presence of two forms of the 9-isomeride in the reduction product of 9-nitrophenanthrene was not recognised until later (J. Schmidt and Heinle, *l.c.*), and there is no information to show whether both forms, or only the α-derivative can be diazotised.

OH in	Hydroxyphenanthrenes and their ethers.	References.
1	Has not been isolated. *Methyl ether*, needles, m.p. 105°–106° ; gives *picrate*, needles, m.p. 153°.	Pschorr, Wolfes and Buckow (Ber. 1900, 33, 162).
2	Forms scales, m.p. 169° ; couples with diazotised bases ; gives *acetate*, needles, m.p. 142°–143°, and *benzoate*, leaflets, m.p. 139°–140°. *Methyl ether*, leaflets, m.p. 100°–101° ; gives *picrate*, needles, m.p. 124°. *Ethyl ether*, leaflets, m.p. 112°.	Werner and Kunz (Ber. 1901, 34, 2524) ; Pschorr and Klein (*ibid.*, 4005) ; Werner and Rekner (Annalen 1902, 321, 305) ; Henstock (Chem. Soc. Trans. 1906, 89, 1528).
3	Forms needles, m.p. 122°–123° ; couples with diazotised bases ; gives *picrate*, m.p. 159°, *acetate*, plates, m.p. 115°–116°, and *benzoate*, needles, m.p. 119°. *Methyl ether*, plates, m.p. 63° ; gives *picrate*, red needles, m.p. 124·5°. *Ethyl ether*, m.p. 46°.	Pschorr, Wolfes and Buckow (*l.c.*) ; Pschorr and Sumuleanu (Ber. 1900, 33, 1821) ; Werner and Kunz (*l.c.*) ; Schmidt (Ber. 1901, 34, 3535) ; Pschorr (*ibid.* 4006).
4	Crystalline, m.p. 106°–109° ; gives *acetate*, leaflets, m.p. 58°–59°. *Methyl ether*, leaflets, m.p. 68° ; gives *picrate*, red needles, m.p. 187°–188°.	Pschorr and Jaeckel (Ber. 1900, 33, 1826) ; Ludewig (Annalen, 1911, 379, 361).
9 (10)	Forms large needles, m.p. 152°–153° ; couples with diazotised bases ; gives *picrate*, red needles, m.p. 183°, *acetate*, needles, m.p. 77°, and *benzoate*, needles, m.p. 96°–97°. *Methyl ether*, needles, m.p. 96°–97°.	Japp and Findlay (Chem. Soc. Trans., 1897, 71, 1115) ; Werner and Frey (Annalen, 1902, 321, 298) ; Pschorr and Schröter (Ber. 1902, 35, 2728).
2 : 3	Has not been isolated. *Dimethyl ether*, leaflets, m.p. 131° ; gives *picrate*, needles, 127°–128°.	Pschorr and Buckow (Ber. 1900, 33, 1829).
3 : 4	Morphol, forms long needles, m.p. 143° ; gives *diacetate*, needles, m.p. 159°. 3-*Methyl ether*, needles, m.p. 65° ; gives *picrate*, red needles, m.p. 150°, and *acetate*, needles, m.p. 131°. 4-*Methyl ether*, oil ; gives *acetate*, needles, m.p. 93°–94°. *Dimethyl ether*, leaflets, m.p. 44° ; gives red *picrate*, m.p. 105°–106°, and *dibromide*, m.p. 123°.	Fischer and Vongerichten (Ber. 1886, 19, 793) ; Knorr (*ibid.* 1892, 25, 1147 ; 1894, 27, 1148) ; Pschorr and Sumuleanu (*ibid.* 1900, 33, 1819, 1823) ; Vongerichten (*ibid.* 352, 1825) ; Knorr (*ibid.* 1904, 37, 3497) ; Knorr and Pschorr (*ibid.* 1905, 38, 3178); Pschorr and Dickhäuser (Annalen, 1910, 373, 81).
9 : 10	Forms needles, m.p. 146° ; gives *monoacetate*, needles, m.p. 168°–170° ; *diacetate*, flat prisms, m.p. 202°, and *dibenzoate* m.p. 230°–231°.	Graebe (Annalen, 1873, 167, 146) ; Japp and Klingemann (Chem. Soc. Trans. 1893, 63, 771) ; Pschorr (Ber. 1902, 35, 2736, 3124), Knesch (D. R.-P. 151981 of 1903.
3 : 4 : 5	Forms scales, m.p. 148°. *Trimethyl ether*, m.p. 90° ; gives *picrate*, brown scales or needles, m.p. 167°.	Vongerichten (Ber. 1906, 39, 1720) ; Pschorr and Koch (Annalen, 1912, 391, 54).
3 : 4 : 6	Has not been isolated. 3-*Methyl ether*, oil ; gives *diacetate*, m.p. 162°–163°. 3 : 6-*Dimethyl ether* (thebaol), m.p. 94° ; gives *acetate*, m.p. 118°–120°. *Trimethyl ether*, oil ; gives *picrate*, m.p. 109°–110°.	Freund (Ber. 1897, 30, 1389) ; Pschorr, Seydel and Stöhrer (*ibid.* 1902, 35, 4406) ; Vongerichten (*ibid.* 4411) ; Knorr (*ibid.* 1904, 37, 3499) ; Pschorr and Rettberg (Annalen, 1910, 373, 66).
3 : 4 : 8	Has not been isolated. 8-Methyl ether ; *diacetate*, m.p. 155°–156°. 3 : 4-*Dimethyl ether*, prisms, m.p. 182°–183°. 4 : 8-*Dimethyl ether* (α-ψ-thebaol), leaflets, m.p. 164°–165° ; gives *acetate*, prisms, m.p. 96°–97°. *Trimethyl ether*, leaflets, m.p. 138° ; gives *picrate*, red needles, m.p. 129°, and *dibromide*, needles, m.p. 139°–140°. 3 : 4-*Dimethyl-8-ethyl ether*, leaflets, m.p. 100° ; gives *picrate*, red needles, m.p. 119°.	Pschorr (Ber. 1900, 33, 183); Pschorr Einbeck and Spangenberg (Ber. 1907, 40, 2000) ; Pschorr and Busch (*ibid.* 2001) ; Knorr and Hoerlein (*ibid.* 2039) ; Pschorr and Loewen (Annalen, 1910, 373, 73) ; Pschorr and Zeidler (*ibid.* 75).
3 : 4 : 9 (or 10)	Has not been isolated. 3-Methyl ether ; *diacetate*, needles, m.p. 202°–204°.	Knorr and Schneider (Ber. 1906, 39, 1420) ; Pschorr, Kuhtz and Roth (*ibid.* 3137).
1 : 3 : 5 : 6	3 : 5 : 6-*Trimethyl ether*, no description given. *Tetramethyl ether*, needles, m.p. 108°–109° gives *picrate*, red needles, m.p. 147°–148°.	Pschorr and Rettberg (*l.c.*) ; Pschorr and Knoeffler (Annalen, 1911, 382, 50.

Among these hydroxyphenanthrenes there are several, about which the information given in the table needs to be supplemented to make clear their properties and relationships.

9- (or 10-) **Hydroxyphenanthrene,** also known as phenanthrone, affords an example of keto-enolic isomerism in the phenanthrene series. It can be obtained from phenanthraquinone by partial reduction with hydriodic acid (Japp and Klingemann, Chem. Soc. Trans. 1893, 63, 770), or from dichlorophenanthrone by reduction with iron and acetic acid (Lachowicz, J. pr. Chem. 1883, [ii.] 28, 168), and is therefore a ketone



$$\begin{array}{c} C_6H_4{\cdot}CO \\ | \qquad | \\ C_6H_4{\cdot}CO \end{array} \rightarrow \begin{array}{c} C_6H_4{\cdot}CH_2 \\ | \qquad | \\ C_6H_4{\cdot}CO \end{array} \leftarrow \begin{array}{c} C_6H_4{\cdot}CCl_2 \\ | \qquad | \\ C_6H_4{\cdot}CO \end{array}$$

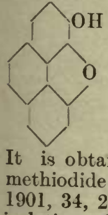
But its formation from phenanthrene-9-sulphonic acid by fusion with caustic alkali, its solubility in alkali, and its conversion into an *ortho*-azo compound (*phenanthraquinonehydrazone,* m.p. 165°) by coupling with diazotised aniline (Werner and Frey, Annalen, 1902, 321, 298), show it to be phenolic under other conditions.

Hydroxyphenanthrenes from opium alkaloids.

The degradation of opium alkaloids into nitrogen compounds containing relatively few carbon atoms and into derivatives of hydroxyphenanthrene free from nitrogen, has been accomplished by Hofmann's method of exhaustive methylation (Ber. 1881, 14, 494, 663), the products being decomposed by hydrogen chloride (Knorr, *ibid.* 1894, 27, 1147), acetic anhydride (Fischer and Vongerichten, *ibid.* 1886, 19, 792), heat (Schrötter and Vongerichten, *ibid.* 1882, 15, 1485), or hot caustic soda solution (Freund, *ibid.* 1897, 30, 1379). A list of decomposition products of this type is given by Knorr and Pschorr, Ber. 1905, 38, 3174. The following summary indicates the sources of the more important nitrogen-free degradation products of opium and *Corydalis* alkaloids.

3 : 4-Dihydroxyphenanthrene or **morphol** is formed when acetylmorphine methiodide and its 3-*methyl ether* when acetylcodeïne methiodide are heated with acetic anhydride (Fischer and Vongerichten, Ber. 1886, 19, 792; Knorr, *ibid.* 1889, 22, 181, 1113; Vongerichten, *ibid.* 1896, 29, 65; 1897, 30, 2439), or morphenol methyl ether is reduced by sodium and alcohol (Vongerichten and Dittmer, *ibid.* 1906, 39, 1719). By the degradation of *apo*morphine the *dimethyl ether* of *morphol-8-carboxylic acid* has been obtained, convertible into morphol dimethyl ether (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4392; Pschorr, Einbeck and Spangenberg, *ibid.* 1907, 40, 1998).

Morphenol (3-hydroxy-4 : 5-phenanthrylene oxide) is the internal anhydride of 3 : 4 : 5-*trihydroxyphenanthrene,* into which it is converted by fusion with caustic alkali (Vongerichten and Dittmer, Ber. 1906, 39, 1718)



$$O : C_{14}H_7{\cdot}OH + H_2O \rightarrow C_{14}H_7(OH)_3.$$

It is obtained from β-methylmorphimethine methiodide (Vongerichten, Ber. 1898, 31, 54; 1901, 34, 2722), or from morphine without the isolation of the morphimethine (Vongerichten, *ibid.* 1900, 33, 358); or from morphenol methyl ether by demethylation with hydriodic acid (Vongerichten, *ibid.* 1898, 31, 3202). It forms needles, m.p. 145°, gives no colouration in alcoholic solution with ferric chloride, dissolves in caustic soda, giving a yellow solution with blue fluorescence, and does not couple with diazotised bases. On reduction it yields *morphol* (Vongerichten, Ber. 1899, 32, 1522).

Its *methyl ether* forms needles, m.p. 65° (*cf.* Knorr, Ber. 1889, 22, 184; Vongerichten, *ibid.* 1898, 31, 54; 1900, 33, 358; Schryver and Lees, Chem. Soc. Trans. 1901, 79, 578); *acetate,* needles, m.p. 140°; and *benzoate,* needles, m.p. 123° (Vongerichten, *l.c.*).

3 : 4 : 6-Trihydroxyphenanthrene. The 3-*methyl ether* is obtained from codeïnone (Knorr, Ber. 1903, 36, 3074), and from codeïnone methiodide (Knorr, *ibid.* 1904, 37, 3501). The 3 : 6-*dimethyl ether* or **thebaol** results from boiling thebaïne with acetic anhydride (Freund, Ber. 1897, 30, 1386), and the *trimethyl ether* when the silver salt of the 8-carboxylic acid, obtained from morphothebaïne, is decomposed by heat (Pschorr and Rettberg, Annalen, 1910, 373, 65).

3 : 4 : 8-Trihydroxyphenanthrene. The 8-*methyl ether* is formed from ψ-*iso*-codeïne methiodide (Knorr and Hoerlein, Ber. 1907, 40, 2039, 3350); and the *trimethyl ether* from the 5-carboxylic acid obtained from thebenine (Pschorr and Loewen, Annalen, 1910, 373, 71).

3 : 4 : 9- (or 10-)Trihydroxyphenanthrene. The *diacetate* of the 3-*methyl ether* is formed when hydroxymethylmorphimethine (Knorr and Schneider, Ber. 1906, 39, 1420) or dichloromethylmorphimethine (Pschorr, *ibid.* 3137) is heated with acetic anhydride.

Vinylhydroxyphenanthrenes.

As primary products of the Hofmann degradation of certain opium and *Corydalis* alkaloids, the following vinylmethoxyphenanthrenes have been obtained, which on oxidation yield the corresponding methoxyphenanthrenecarboxylic acids.

5-*Vinyl*-3 : 4 : 8-*trimethoxyphenanthrene,* from thebenine, forms tablets, m.p. 122·5°; *picrate,* red tablets, m.p. 110° (Pschorr and Massaciu, Ber. 1904, 37, 2789). The 8-*ethoxy* derivative forms plates, m.p. 78° (Pschorr and Loewen, Annalen, 1910, 373, 72).

8-*Vinyl*-3 : 4-*dimethoxyphenanthrene,* from *apo*morphine, forms rhombic prisms, m.p. 80°; *picrate,* violet needles, m.p. 128° (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4391; *cf.* Pschorr, *ibid.* 1906, 39, 3124).

8-*Vinyl*-3 : 4 : 6-*trimethoxyphenanthrene,* from morphothebaïne, forms prisms, m.p. 60°–61°; *picrate,* reddish-violet needles, m.p. 125°–126° (Knorr and Pschorr, Ber. 1905, 38, 3157; Pschorr and Rettberg, Annalen, 1910, 373, 65).

8-*Vinyl*-3 : 4-*dimethoxy*-5 : 6-*methylenedioxyphenanthrene,* from bulbocapnine, forms yellow needles, m.p. 101° (Gadamer and Kuntze, Arch. Pharm. 1911, 249, 630).

PHENANTHRENECARBOXYLIC ACIDS.

Phenanthrenecarboxylic acids have been prepared by hydrolysis of the nitriles obtained from the three phenanthrenesulphonic acids on distillation with potassium cyanide or ferrocyanide (Schultz and Japp, Ber. 1877, 10, 1661; Japp, Chem. Soc. Trans. 1880, 37, 83; Werner and Kunz, Annalen, 1902, 322, 323). Synthetically Pschorr has obtained the 9-carboxylic acid (Ber. 1896, 29, 496), and the 8 : 9-dicarboxylic acid, the latter of which readily forms a well-crystallised anhydride (m.p. 283°–284°), and exhibits the behaviour of a naphthalene *peri-* derivative (*ibid.* 1906, 39, 3107).

Phenanthrene-2-carboxylic acid, needles, m.p. 254°; *nitrile*, granules, m.p. 105°; forms *phenanthraquinone-2-carboxylic acid* on oxidation.

Phenanthrene-3-carboxylic acid ([α-] acid), scales, m.p. 269°, forms the *barium* salt, $BaA_2,7H_2O$, sparingly soluble needles; *sodium* salt, $NaA,4H_2O$, easily soluble scales; *amide*, scales, m.p. 227°–228°; *nitrile*, needles, m.p. 102°; and yields *phenanthraquinone-3-carboxylic acid* on oxidation.

Phenanthrene-9-(10-)carboxylic acid ([β-] acid), needles, m.p. 250°–252°, gives the *barium* salt $BaA_2,6H_2O$, sparingly soluble tablets; *sodium* salt, $NaA,5H_2O$, easily soluble rhombic tablets; *amide*, needles, m.p. 226°; *nitrile*, needles, m.p. 103°; and yields *phenanthraquinone* on oxidation.

HYDROXYPHENANTHRENECARBOXYLIC ACIDS.

Hydroxyphenanthrenecarboxylic acids have been obtained (*a*) from hydroxyphenanthrenes by the Kolbe method with carbon dioxide; (*b*) from alkaloids by oxidation of vinylhydroxyphenanthrenes; (*c*) synthetically by Pschorr's method from substituted cinnamic acids. As will be seen from the following summary, in few cases only have salts been analysed, or esters described.

(i) **Hydroxyphenanthrenecarboxylic acids,** $[OH : CO_2H]$.

2 : 3 (?). Yellow needles, m.p. 277° (decomp.); *acetate*, needles, m.p. 210° (Werner and Kunz, Ber. 1902, 35, 4425); *methyl* ester, needles, m.p. 126°.

2 : 9 Prisms, m.p. 278°; *acetate*, plates, m.p. 223° (Pschorr and Quade, Ber. 1906, 39, 3123).

3 : 2 (?) Yellow prisms, m.p. 303° (decomp.); *acetate*, needles, m.p. 207°–208°: *methyl* ester, needles, m.p. 171° (Werner and Kunz, *l.c.*).

(ii) **Methoxyphenanthrenecarboxylic acids,** $[OMe : CO_2H]$.

2 : 9 Colourless needles, m.p. 228° (Pschorr, Ber. 1901, 34, 4002).

4 : 9 Needles, m.p. 224° (Pschorr and Jaeckel, Ber. 1900, 33, 1827).

1 : 10 Yellow leaflets, m.p. 215° (Pschorr, Wolfes and Buckow, Ber. 1900, 33, 169).

3 : 10 Needles, m.p. 239° (*ibid.* 174).

(iii) **Hydroxymethoxyphenanthrenecarboxylic acids,** $[OH : OMe : CO_2H]$.

3 : 4 : 9 Needles, m.p. 214°–216° (Pschorr and Sumuleanu, Ber. 1900, 33, 1822).

4 : 3 : 9 Needles, m.p. 264°; *acetate*, m.p. 244° (Pschorr and Vogtherr, Ber. 1902, 35, 4414).

(iv) **Dimethoxyphenanthrenecarboxylic acids,** $[OMe : OMe : CO_2H]$.

2 : 3 : 9 Needles, m.p. 270° (Pschorr and Buckow, Ber. 1900, 33, 1830).

3 : 4 : 8 Yellow needles, m.p. 196°; *ethyl* ester, prisms, m.p. 81°–83°; *hydrazide*, needles, m.p. 194°–195° (Pschorr, Jaeckel and Fecht, Ber. 1902, 35, 4392; Pschorr, Einbeck and Spangenberg, *ibid.* 1907, 40, 1999).

3 : 4 : 9 Needles, m.p. 227°–228° (Pschorr and Sumuleanu, Ber. 1900, 33, 1819).

(v) **Hydroxydimethoxyphenanthrenecarboxylic acids.** $[OH : OMe : OMe : CO_2H]$.

3 : 4 : 8 : 9 Six-sided plates, m.p. 231°; *acetate*, prisms, m.p. 220°–227° (Pschorr, Ber. 1900, 33, 180).

4 : 3 : 6 : 9 Leaflets, m.p. 254°–256°; *acetate*, m.p. 201°–203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4409).

8 : 3 : 4 : 9 Needles; *lactone*, needles, m.p. 160° (Pschorr and Popovici, Ber. 1906, 39, 3120).

(vi) **Trimethoxyphenanthrenecarboxylic acids,** $[OMe : OMe : OMe : CO_2H]$.

3 : 4 : 5 : 9 Prisms, m.p. 234°–235° (Pschorr, Zeidler and Dickhäuser, Annalen, 1912, 391, 47; Pschorr and Koch, *ibid.* 53).

3 : 4 : 6 : 8 Needles, m.p. 201°; *methyl* ester, needles, m.p. 101°–102°; *ethyl* ester, leaflets, m.p. 83°–84° (Knorr and Pschorr, Ber. 1905, 38, 3158; Pschorr and Rettberg, Annalen, 1910, 373, 51).

3 : 4 : 6 : 9 Yellow needles, m.p. 203° (Pschorr, Seydel and Stöhrer, Ber. 1902, 35, 4406).

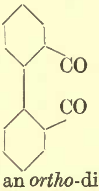
3 : 4 : 7 : 9 Needles, m.p. 214° (Pschorr, Zeidler and Dickhäuser, *l.c.*).

3 : 4 : 8 : 5 Needles, m.p. 224°–226° (Pschorr and Massaciu, Ber. 1904, 37, 2790; Pschorr and Loewen, Annalen, 1910, 373, 70). The 8-*ethoxy* acid forms needles, m.p. 191°.

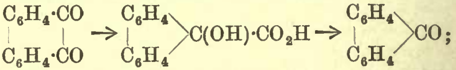
3 : 4 : 8 : 9 Leaflets, m.p. 250° (Pschorr and Busch, Ber. 1907, 40, 2003). The 8-*ethoxy* acid forms leaflets, m.p. 265° (Pschorr and Zeidler, Annalen, 1910, 373, 78).

(vii) **3 : 4-Dimethoxy-5 : 6-methylenedioxyphenanthrene-8-carboxylic acid**, needles, m.p. 228° (Gadamer and Kuntze, Arch. Pharm. 1911, 249, 630).

DIHYDROPHENANTHRENE DERIVATIVES.



Phenanthraquinone is a typical member of the series of *ortho*-quinones, but unlike [β-]naphthaquinone, to which it shows a close resemblance in properties, it can be obtained from the corresponding hydrocarbon by direct oxidation. It gives the characteristic reactions of an *ortho*-diketone, as may be seen by comparison with benzil; thus it reacts with hot caustic alkali solution, forming a glycollic acid, which by oxidation is converted into a ketone:



$$\begin{array}{l}C_6H_4\cdot CO\\ \ |\\ C_6H_4\cdot CO\end{array} \rightarrow \begin{array}{l}C_6H_4\\ \ |\\ C_6H_4\end{array}\!\!>C(OH)\cdot CO_2H \rightarrow \begin{array}{l}C_6H_4\\ \ |\\ C_6H_4\end{array}\!\!>CO;$$

yields azines by condensation with *ortho*-diamines; and gives a mono- and a di-oxime with hydroxylamine. The relationship between the colour and constitution of the dioxime and its derivatives has been discussed by Schmidt and Söll (Ber. 1907, 40, 2454; *cf.* Hantzsch and Glover, *ibid.* 4344; Schmidt and Mezger, *ibid.* 4560).

Substitution derivatives of phenanthraquinone are formed either by oxidising the corresponding phenanthrene derivatives (other than 9-, 10-, or 9 : 10- compounds), or by direct substitution. In the latter case substitution usually occurs in the equivalent 2- and 7-positions, thus recalling the formation of *meta*-derivatives of benzene under the directing influence of the carbonyl radicle.

Preparation.—Crude phenanthrene (100 grams), consisting of the easily soluble constituents of the coal-tar fraction boiling at 320°–340°, is warmed with a solution of potassium dichromate (300 grams) in sulphuric acid (900 grams), diluted with water (1·5 litres), and, after the vigorous reaction has subsided, more dichromate (300 grams) is added gradually, the liquid finally being boiled for some time. After precipitation by water the quinone is washed, dried, stirred into concentrated sulphuric acid, and after 24 hours mixed with water. Chromium salts, diphenic acid, acridine, &c., pass into solution, the last traces of organic acids or hydrocarbons being removed by extracting the residue with cold, dilute caustic soda solution, and afterwards (when dry) with ether. The residue is freed from anthraquinone by digestion with warm concentrated sodium bisulphite solution in which the phenanthraquinone dissolves, and the filtrate poured into a solution of potassium dichromate in dilute sulphuric acid;

the precipitate is then washed, dried, and crystallised from alcohol or coal-tar hydrocarbons (Anschütz and Schultz, Annalen, 1879, 196, 38). Or it may be made by oxidising purified phenanthrene with chromium trioxide in hot acetic acid solution and purified by means of the sodium bisulphite compound (Graebe, Annalen, 1873, 167, 140).

Electrolytically it can be obtained by passing the calculated amount of a current of 1 to 2 amp. per sq. in. through a suspension of phenanthrene in 20 p.c. sulphuric acid, containing about 2 p.c. of cerium sulphate, at 40°–60° (Meister, Lucius and Brüning, D. R.-P. 152063; Eng. Pat. 19178 of 1902).

Properties.—It crystallises in tufts of long yellow needles, m.p. 205° (Graebe, *l.c.*), boils above 360° without decomposition, sublimes in orange-red prisms, but is odourless and nonvolatile with steam. It is only very slightly soluble in water, but dissolves readily in hot alcohol, benzene, or acetic acid. With concentrated sulphuric acid in the cold it gives a green solution, but if benzene containing thiophen be present, the colour is bluish-green, and the liquid, when poured into water and shaken out with ether, gives to the ethereal solution a characteristic reddish-violet colouration, the limit of sensitiveness being reached with 0·0005 gram of the quinone (Laubenheimer, Ber. 1875, 8, 224; Meyer, *ibid.* 1883, 16, 1624, 2972).

Reactions.—(1) Phenanthraquinone, unlike anthraquinone, dissolves in warm sodium bisulphite solution,[1] and is readily reduced to the *hydroquinone* by warming it with sulphurous acid (Graebe, *l.c.*), or sulphuretted hydrogen, or phenylhydrazine acetate (Schmidt and Kämpf, Ber. 1902, 35, 3124).

(2) When boiled with fuming hydriodic acid it is reduced to 9-*hydroxyphenanthrene* (Japp and Klingemann, Chem. Soc. Trans. 1893, 63, 770).

(3) With hydroxylamine it forms a *monoxime*, golden-yellow needles, m.p. 158° (Meyer and Auwers, Ber. 1889, 22, 1989), and a *dioxime*, yellow prisms, m.p. 202° (Meyer and Auwers, *l.c.*; Schmidt and Söll, Ber. 1907, 40, 2455), apparently without the production of stereoisomerides. The *anhydride* of the dioxime forms colourless needles, m.p. 186°–187° (Schmidt and Söll, *l.c.*).

(4) With phenylhydrazine it gives a *hydrazone*, dark red scales, m.p. 162°–163° (Zincke, Ber. 1883, 16, 1564; Werner and Frey, Annalen, 1902, 321, 304), but in the absence of a solvent the product is phenanthroxazine $C_{28}H_{17}ON$ (Bamberger and Grob, Ber. 1901, 34, 535).

(5) When boiled with caustic potash solution it is converted into *diphenyleneglycollic acid*[2] (Friedlaender, Ber. 1877, 10, 126, 534; *cf.* Schmidt and Bauer, *ibid.* 1905, 38, 3757), or with caustic alkali solution and permanganate into *diphenyleneketone* (Anschütz and Japp, *ibid.* 1878, 11, 211), but when boiled with methyl alcoholic potash it gives *diphenic acid* (Meyer and Spengler, *ibid.* 1905, 38, 443), or with alcoholic potash *diphenic acid* (Anschütz and Schultz, Annalen, 1879, 196, 49) and an orange-coloured *lactone* $C_{16}H_8O_3$, m.p. 220°–221° (Meyer and Spengler, *l.c.*).

(6) When distilled with soda-lime it yields *diphenyl* (Graebe, *l.c.*), but with caustic lime the products are *diphenyleneketone*, *fluorene alcohol*, and a small quantity of *fluorene* (Anschütz and Schultz, *l.c.*).

(7) With phenols, by prolonged boiling with acetic acid and sodium acetate, it yields additive products which are crystalline and either colourless or yellow (Deichler, D. R.-P. 109344 of 1898).

(8) It forms condensation products with many substances, some of which have been introduced as dyestuffs, but probably have no technical importance. For example, it has been condensed with arylhydrazinesulphonic acids. (Akt. f. Anilinfab. D. R.-P. 40745; Eng. Pat. 6688 of 1887); with mono- alkyl- (or aryl-)*ortho*-phenylenediamines (Bad. Anilin- u. Soda-Fab. D. R.-P. 90212; Eng. Pat. 15953 of 1896), or 1 : 2- or 2 : 3-diaminoanthraquinone (Bayer & Co. D. R.-P. 170562 of 1904; *cf.* Scholl and Kačer, Ber. 1904, 37, 4532) forming *azines*; with dialkyl-*p*-phenylenediaminethiosulphonic acids forming blue *thiazines* (Fries, D. R.-P. 126963 of 1901); and with *p*-amino-*m*-hydroxydialkylanilines forming blue *oxazines* (Fries, D. R.-P. 130743 of 1901).

Bromo derivatives (*cf.* Schmidt, Ber. 1904, 37, 3551). When bromine is added to phenanthraquinone, mixed with sufficient water to form a paste at 0°, a *dibromide* $C_{14}H_8O_2Br_2$ is formed, m.p. 98° (Schmidt and Junghaus, *ibid.* 3556), which, when boiled with water, reverts mainly to the quinone. The minor product of the debromination, 2-*bromophenanthraquinone*, needles, m.p. 233°, is better prepared by brominating the quinone under pressure at 100° (*ibid.* 3358). By further bromination at 150°–160° 2 : 7-*dibromophenanthraquinone*, needles, m.p. 323°, is obtained (*ibid.* 3567).

Nitro derivatives (*cf.* Schmidt, Ber. 1903, 36, 3726). When phenanthraquinone is boiled with concentrated nitric acid for 2 minutes it is converted into a mixture of 2-*nitrophenanthraquinone*, golden yellow scales, m.p. 257°–258° (Anschütz and Schultz, Ber. 1876, 9, 1404; Schmidt and Austin, *ibid.* 1903, 36, 3731), and 4-*nitrophenanthraquinone*, yellow needles, m.p. 179°–180° (Schmidt and Kämpf, *ibid.* 3734). The 3-*nitrophenanthraquinone*, orange needles, m.p. 279°–280°, is obtained from 3-nitrophenanthrene by oxidation (Schmidt and Kämpf, Ber. 1902, 35, 3119) or from 9-bromophenanthrene (Austin, Chem. Soc. Trans. 1908, 93, 1762), or from 9 : 10-diaminophenanthrene (Schmidt and Söll, Ber. 1908, 41, 3684) by nitration.

If phenanthraquinone be further nitrated, the products are 2 : 7-*dinitrophenanthraquinone*, yellow needles, m.p. 300°–303° (Graebe, Annalen, 1873, 167, 144; Schmidt and Kämpf, Ber. 1902, 35, 3122; 1903, 36, 3738), and 4 : 5-*dinitrophenanthraquinone*, brownish-yellow needles, m.p. 228° (Schmidt and Kämpf, *l.c.* 3745).

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[1] The bisulphite compound, $C_{14}H_8O_2,NaHSO_3,2H_2O$ (Graebe, *l.c.*), on reduction in aqueous solution with zinc dust, also yields 9 : 10-dihydroxyphenanthrene (Knesch, D. R.-P. 151981 of 1903).

[2] According to Schmidt and Bauer (Ber, 1905, 38, 3737) the production of fluorene derivatives (glycollic acids) by means of 10 p.c. caustic potash solution proceeds, in the case of phenanthraquinone, only with difficulty at 80°, but in that of 2-nitro- or 4-nitrophenanthraquinone more easily (at 50° and 65° respectively), and in that of 2 : 7-dinitro- or 4 : 5-dinitro-phenanthraquinone readily at the ordinary temperature.

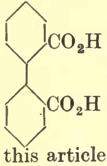
Amino derivatives. 2-*Aminophenanthraquinone*, violet needles, m.p. above 320° (Werner, Annalen, 1902, 321, 338); 3-*aminophenanthraquinone*, dark red needles, m.p. 254° (Werner, *l.c.*; Schmidt and Söll, Ber. 1908, 41, 3694); 2 : 7-*diaminophenanthraquinone*, violet needles, m.p. above 310° (Anschütz and Meyer, Ber. 1885, 18, 1944); and 4 : 5-*diaminophenanthra*quinone, indistinct crystals, m.p. 235°, which, like 1 : 8-diaminonaphthalene, does not form condensation products (Schmidt and Kämpf, *ibid.* 1903, 36, 3750), have been described.

Hydroxy derivatives. The amino- and diamino-phenanthraquinones can be diazotised without difficulty, forming the corresponding *hydroxyphenanthraquinones* (*cf.* Werner, Annalen, 1902, 322, 138, 159; Schmidt and Kämpf, *l.c.*; Schmidt and Leipprand, Ber. 1905, 38, 3733). Owing to its relationship to morphine, and the resemblance of some of its properties to those of alizarin, the most interesting of these is:

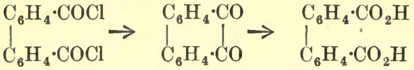
Morpholquinone (3 : 4-*dihydroxyphenanthraquinone*). This quinone has been obtained from diacetylmorphol by oxidation, followed by deacetylation (Vongerichten, Ber. 1899, 32, 1521), and from 3-hydroxyphenanthrene by nitration, reduction, and diazotisation (Schmidt and Söll, *ibid.* 1908, 41, 3699). It forms yellowish-brown needles; gives a *diacetate*, yellow needles, m.p. 196°; and, unlike its isomerides and its monomethyl ether, but like alizarin (*q.v.*), forms lakes which with aluminium salts are blue, and with chromium salts deep violet in colour (Vongerichten, *l.c.*). On oxidation it yields phthalic acid.

Diphenyl Derivatives.

Diphenic acid (*diphenyl*-2 : 2′-*dicarboxylic acid*).



From the formula of the hydrocarbon diphenyl, the existence of 15 diphenyldicarboxylic acids can be predicted, but the acids actually known number only about one-third of these, and of them diphenic acid alone requires description in this article. Diphenic acid is closely related to phenanthraquinone; it was first obtained from this substance by oxidation (Fittig and Ostermayer, Annalen, 1873, 166, 367), and its chloride, on reduction with zinc and hydrochloric acid, forms 9 : 10-dihydroxyphenanthraquinone or its oxidation product—phenanthraquinone (Graebe and Aubin, Annalen, 1888, 247, 268).



$$\begin{array}{c} C_6H_4\cdot COCl \\ | \\ C_6H_4\cdot COCl \end{array} \rightarrow \begin{array}{c} C_6H_4\cdot CO \\ |\quad\;| \\ C_6H_4\cdot CO \end{array} \rightarrow \begin{array}{c} C_6H_4\cdot CO_2H \\ | \\ C_6H_4\cdot CO_2H \end{array}$$

Preparation.—A solution of phenanthraquinone (1 part) in sulphuric acid (6 parts) is poured slowly with constant stirring into a solution of potassium dichromate (4 parts) in water (10 parts), whereby the quinone is precipitated in a fine state of division. The heat of dilution of the sulphuric acid is sufficient to start the oxidation, and the reaction is completed by boiling the mixture vigorously during 4 hours in a reflux apparatus; the acid being extracted from the precipitate by sodium carbonate solution (Götz, Monatsh. 1902, 23, 27; Graebe and Aubin, *l.c.*; Schmitz, Annalen, 1878, 193, 116). Diphenic acid also can be obtained by boiling phenanthraquinone with aqueous or alcoholic potash (Anschütz and Schultz, Annalen, 1879, 196, 49; Meyer and Spengler, Ber. 1905, 38, 443).

Properties.—It crystallises in scales or monoclinic prisms, m.p. 228°–229° (Schultz, Annalen, 1880, 203, 97), sublimes in needles, is moderately soluble in hot water, and dissolves readily in alcohol or ether. Dehydrating agents convert it into the *anhydride*; but, when heated with caustic lime, it forms *diphenyleneketone* (*cf.* Schmitz, *l.c.*; Kerp, Ber. 1896, 29, 228), or with slaked lime or soda-lime, *diphenyl* (Anschütz and Schultz, *l.c.*).

Derivatives.—The *barium*, $BaA,4H_2O$, *calcium*, $CaA,2\frac{1}{2}H_2O$, and *magnesium*, $MgA,4H_2O$, salts are crystalline (Fittig and Ostermayer, *l.c.*). The *dimethyl* ester, conveniently prepared from methyl *o*-iodobenzoate and copper powder (Ullmann, Annalen, 1904, 322, 70), forms monoclinic prisms, m.p. 74·5° (Schultz, *l.c.*), and the *diethyl* ester, cubes, m.p. 42° (Hummel, Annalen, 1878, 193, 129). The *chloride* is crystalline, m.p. 93°–94° (Graebe and Aubin, *l.c.*); the *anhydride* forms needles, m.p. 217° (Anschütz, Ber. 1877, 10, 1184; Graebe and Mensching, *ibid.* 1880, 13, 1302; Graebe and Aubin, *l.c.*); and the *imide*, needles, m.p. 219°–220° (Graebe and Aubin, *l.c.*; Wegerhoff, Annalen, 1889, 252, 16).

4 : 4′-Diaminodiphenyl-2 : 2′-dicarboxylic acid (*m-diaminodiphenic acid*) is obtained by boiling *m*-hydrazobenzoic acid with concentrated hydrochloric acid (Griess, Ber. 1884, 7, 1069); or, mixed with the 4 : 2′-dicarboxylic acid, by reducing *m*-nitrobenzoic acid with zinc dust and caustic soda, afterwards extracting the product with hydrochloric acid (Meister, Lucius and Brüning, D. R.-P. 69541 of 1892); or by reducing 4 : 4′-dinitrodiphenic acid (producible from 2 : 7-dinitrophenanthraquinone by oxidation) with tin and hydrochloric acid (Struve, Ber. 1877, 10, 76; Schultz, *l.c.*).

Properties.—The *acid*, $H_2A,1\frac{1}{2}H_2O$, forms needles, sparingly soluble in water or alcohol, and the *hydrochloride* $H_2A,2HCl$, prisms, sparingly soluble in cold water. When heated with lime it yields *diaminofluorene*, but when the barium salt is heated *benzidine* is obtained. From the *tetrazo* compound *disazo* dyes have been made (Paul, D. R.-P. 41819 of 1886; Eng. Pat. 8296 of 1887; Beyer and Kegel, D. R.-P. 44089; 44161 of 1887); but not being direct cotton dyes, they have no technical value. In this respect the disazo dyes from this source differ from those produced by coupling diazotised 4 : 4′-diaminodiphenyl-3 : 3′-dicarboxylic acid (*o*-diaminodiphenic acid) with the same naphthylamine- or naphthol-sulphonic acids, which are direct cotton dyes, although no longer of any value (Bad. Anilin- u. Soda-Fab. D. R.-P. 43524 of 1886; 54662; Eng. Pat. 9676 of 1890). W. P. W.

PHENANTHRONAPHTHAZINE *v.* Azines.

PHENANTHROPHENAZINE *v.* Azines.

PHENAZINE *v.* Azines.

PHENEGEL *v.* Synthetic drugs.

p-**PHENETIDINE** (*p-aminophenetole*) may be obtained by the action of alcoholic sulphuric, or hydrochloric acid, on phenylhydroxylamine (Bamberger and Lagutt, Ber. 1898, 31, 1560). It may be prepared by adding 212 grams *p*-nitrophenetole gradually to a solution of 848 grams of stannous chloride in 1060 of hydrochloric acid at 50°–60°. It is then precipitated from solution as the hydrochloride by the addition of concentrated hydrochloric acid (Paul, Zeitsch. angew. Chem. 1896, 587).

p-Phenetidine may also be prepared by treating *p*-azophenetole with tin and hydrochloric acid (D. R. P. 48543); or by heating benzylidene-*p*-aminophenol with ethyl bromide and alcoholic sodium hydroxide for 3 hours. The product is then warmed with acid when *p*-phenetidine separates (D. R. P. 69006).

p-Phenetidine is a liquid, b.p. 254·2°–254·7°, m.p. 2·4° (Schneider, Zeitsch. physikal. Chem. 1896, 19, 155). When heated with hydrogen peroxide and dilute sulphuric acid, it yields a brown colouring matter $C_{24}H_{22}N_2O_5$, but when oxidised in the cold with a permanganate it yields quinone, carbon dioxide, acetic and oxalic acids, and resinous substances (Kinzel, Arch. Pharm. 229, 329). When to an alcoholic solution, 5 c.c. of a potassium iodide solution are added and the mixture is heated, a rose-red colour is formed (Goldmann, Pharm. Zeit. 1893, 36, 208). For the detection of phenetidine in urine *see* Edlefsen, Chem. Zentr. 1900, i. 573.

p-Phenetidine sulphonic acid is prepared by heating the hydrogen sulphate of the base or by boiling *p*-nitrophenetole with sodium hydrogen sulphite. It forms readily crystalline sodium salts, and may be diazotised and joined with β-naphthol, thus obtaining the azo- compounds which with barium and aluminium hydroxides form red lakes of great brilliancy and fastness (D. R. P. 146655; *see* also D. R. P. 189469). *p*-Phenetidine sulphonic acid may also be obtained by heating phenetidine with fuming sulphuric acid (Eng. Pat. 14375, 1897; *see* also Cohn, Annalen, 1899, 309, 234; Paul, *l.c.*).

Ethyl sulphone phenetidine

$$EtO{\cdot}C_6H_4{\cdot}NHSO_2{\cdot}C_2H_5$$

is obtained by the action of ethyl sulphochlorides on *p*-phenetidine. It forms shining white leaflets, m.p. 80°–81°, and acts as a monobasic acid, forming well-crystallised salts which may be employed in medicine as they have antineuralgic, antipyretic, sedative and hypnotic properties (Autenrieth and Bernheim, Arch. Pharm. 1904, 242, 579). Similar aromatic sulpho derivatives, also employed in medicine, have been prepared (Eng. Pat. 3791, 1896).

By the interaction of *p*-phenetidine and its homologues with ethyl orthoformate, compounds are formed of the type of methenyldi-*p*-phenetidine, which possess anæsthetic properties (Goldschmidt, Chem. Zeit. 1902, 26, 745; J. Soc. Chem. Ind. 1890, 650).

The following derivatives of *p*-phenetidine also have medicinal properties:—

The *citrates*, *tartrates*, and *mandelates* prepared by mixing the theoretical quantities of the acid and base dissolved in suitable solvents (Eng. Pat. 11288, 1895).

Lactyl-p-phenetidine (*lactophenin*) is prepared by heating benzylidene *p*-phenetidine with lactic acid (Eng. Pat. 19188, 1894; *see* also Eng. Pat. 29869, 1896). It forms colourless prisms. The *diacetate of p-phenetidine*, m.p. 55°–56°, b.p. 182°/12 mm. is obtained by heating phenacetin (p-*phenetidine monoacetate*) with a large excess of acetic anhydride (D. R. P. 75611; Bistrzycki and Ulffers, Ber. 1898, 31, 2788; Cohn, *ibid.* 1899, 32, 2239). *Benzyl*-p-*phenetidine*, m.p. 45°–46°, obtained by heating benzyl chloride with *p*-phenetidine forms crystalline plates (Wenghöffer, Chem. Zeit. 19, 1753; Wedekind and Fröhlich, Ber. 1907, 40, 1001). *Ethoxyphenyloxamide* $(CO)_2(NH{\cdot}C_6H_4{\cdot}OEt)_2$ by heating anhydrous oxalic acid with *p*-phenetidine to 140°–145°. It forms thin needles, m.p. 263° (Wenghöffer, *l.c.*).

Amygdalyl phenetidine by heating *p*-phenetidine mandelate to 170°, forms shining white plates, m.p. 140·5° (Wenghöffer, *l.c.*). *Ethyl β-pheneldyl crotonate* obtained by condensing *p*-phenetidine with ethyl acetoacetate, forms, when heated rapidly, to 225°–240°, p-*ethoxy-γ-hydroxyquinaldine* $EtOC_6H_3{\cdot}NCCH_3{\cdot}C(OH){\cdot}CH$, which has powerful antipyretic properties (Wenghöffer, *l.c.*). *Salicyl*-p-*phenetidene* (*Saliphen*), m.p. 142°–143°, is prepared by heating the constituents with phosphorus oxychloride; its *aceto* derivative has m.p. 92° (U.S. Pats. 706355, 706356, 1902; Bolezzi, Gazz. chim. ital. 1898, 28, ii. 197). Also *amino acet*-p-*phenetidine* (*Phenocoll*), *valeryl*-p-*phenetidine* (*Sedatin*), *vanillin*-p-*phenetidine*, and the *furfural*, *propionyl*, *methyl glycolic*, and *acetosulphonic* derivatives (J. Soc. Chem. Ind. 1898, 726; Eng. Pat. 14954, 1896; 4565, 1905).

For the *halogen* derivatives, *see* Staedel (Annalen, 1883, 217, 55); Reverdin (Ber. 1896, 29, 2595); Reverdin and Düring (*ibid.* 1899, 32, 152); Grothe (Arch. Pharm. 1900, 238, 587, 600). Nitro derivatives are described by Wender (Gazz. chim. ital. 19, 218); Autenreith and Hinsberg (Arch. Pharm. 229, 456); Blanksma (Rec. trav. chim. 1905, 24, 40).

For other derivatives, *see* Boettinger (Arch. Pharm. 1896, 234, 158); Wirths (*ibid.* 620); Meves (J. pr. Chem. 1900, [ii.] 61, 449); Vorländer (Annalen, 1897, 294, 273, 302); Bischoff (Ber. 1898, 31, 3241, 3248); Partheil and Schumacher (*ibid.* 591); Sachs and Levy (*ibid.* 1904, 37, 874); Schroeter (*ibid.* 1905, 38, 3181); Bischoff and Fröhlich (*ibid.* 1906, 39, 3976); Erlenmeyer (*ibid.* 791); Goldschmidt (Chem. Zeit. 1901, 25, 178); Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123); Fourneau (J. Pharm. Chim. 1910, [vii.] 1, 97).

o-Phenetidine is produced as a by-product in the formation of the para- compound.

PHENETOLE $C_6H_5{\cdot}O{\cdot}C_2H_5$.

Preparation.—Phenetole can be obtained by heating potassium phenate with ethyl iodide (Cahours, Ann. Chim. Phys. [iii.] 27; 463), or by heating a mixture of equal parts of phenol and phosphorus pentoxide at 200° and gradually adding alcohol (Kastropp, Ber. 1877, 10, 1685). It is prepared by heating molecular proportions of crude calcium or sodium sulphovinate and sodium phenate (prepared by mixing molecular proportions of phenol and aqueous caustic soda of sp.gr. 1·33) at 150° for some hours (Kolbe, J. pr. Chem. [ii.] 27, 424).

It may also be prepared by fusing perfectly dry sodium ethoxide with perfectly dry phenyl sulphonate (Moureu, J. Pharm. Chim. 1898, 8, 211); by the action of sodium ethoxide on triphenyl phosphate (Morel, Compt. rend. 1899, 128, 508); or by passing alcohol into a mixture of phenol and β-naphthalene sulphonate heated to 120°–140° (D. R.-P. 76574; Frdl. iv. 18).

Properties.—It is a colourless, aromatic liquid, insoluble in water, but soluble in alcohol or ether. It boils at 172° (Cahours), at 171·5°–172·5° at 762·4 mm. (Schiff, Annalen, 1883, 220, 105), and melts at −33·5°.

When phenetole is heated with sulphuric acid or left to stand at ordinary temperatures, p-*phenetole sulphonic* acid, together with a little of the meta-acid separates (Shober and Bowers, Amer. Chem. J. 1901, 25, 69).

Other sulphur compounds of phenetole are described by Gattermann, Ber. 1899, 32, 1136; Taboury, Bull. Soc. chim. 1905, [iii.] 33, 836; Smiles and Rossignol, Chem. Soc. Trans. 1908, 756.

Alkyl phenetoles are obtained by treating a mixture of iodophenetole and ethyl iodide with sodium in benzene solution (Jannasch and Hinrichsen, Ber. 1898, 31, 1824).

Phenetoleazobenzaldehyde sulphonic acid, $C_2H_5O{\cdot}C_6H_4{\cdot}N{:}NC_6H_3(SO_3H)CHO$, is prepared by oxidizing the dye 'Chrysophenin G' with cold aqueous permanganate (Eng. Pat. 1431, 1898). It forms orange-coloured microscopic crystals sparingly soluble in cold, readily in hot water.

By reacting with amino compounds a series of phenetole azo-methineazo dyes have been prepared (Green and Sen, Chem. Soc. Trans. 1910, 2242; *v.* also AZO-DYES).

Phenetole azo-phenols have been prepared by Jacobson and Meyer (Annalen, 1895, 287, 212); Hewitt, Moore, and Pitt (Ber. 1898, 31, 2114; Chem. Soc. Proc. 1897, 157); *v.* also Naegali (Bull. Soc. chim. 1894, [iii.] 11, 897).

The following derivatives have also been prepared:—

Halogen phenetoles (Autenrieth, Arch. Pharm. 1895, 233, 26; Bentley, Haworth, and Perkin, Chem. Soc. Trans. 1896, 165; Reverdin, Ber. 1896, 29, 2595; Jannasch and Naphtali, Ber. 1898, 31, 1714; Grignard, Compt. rend. 1904, 138, 1048; Autenrieth and Mühlinghaus, Ber. 1906, 39, 4098; Bonneaud, Bull. Soc. Chim. 1910, [iv.] 7. 776).

p-Iodohydroxy phenetole explodes at 225° and has strong oxidising and antiseptic properties (D. R. P. 161725).

Nitro-phenetoles (Lobry de Bruyn, Rec. trav. chim. 13, 101; Blanksma, *ibid.* 1904, 23, 119; *ibid.* 1905, 24, 40; *ibid.* 1908, 27, 49; Paul, Zeitsch. angew. Chem. 1896, 587; Jacobson and Hönigsberger, Ber. 1903, 36, 4124; Blanksma, Proc. k. Akad. Wetensch. Amsterdam, 1908, 10, 509; Chem. Weekblad, 1908, 5, 789).

Halogen nitro-phenetoles (Jackson and Calhane Amer, Chem. J. 1902, 28, 451; Jackson and Gallivan, *ibid.* 1898, 20, 179; Jackson and Fiske, *ibid.* 1903, 30, 53; Reverdin, *l.c.*). *Nitroso phenetoles* (Rising, Ber. 1904, 37, 43).

Phenetole also forms compounds with tellurium chloride and with selenium (Rust, Ber. 1897, 30, 2828; Kunckell, *ibid.* 1895, 28, 609).

For some other derivatives of phenetole *v.* Tust and Gattermann (Ber. 1892, 25, 3528); Pechman and Wedekind (*ibid.* 1895, 28, 1688); Wiechell, Annalen, 1894, 279, 337; Dzierzgowski (J. Russ. Phys. Chem. Soc. 25, 275); Tröger and Volkmer (J. pr. Chem. 1905, [ii.] 71, 236); Tröger and Vasterling (*ibid.* 72, 323).

PHENOCOLL *v.* SYNTHETIC DRUGS.

PHENOCYANINES *v.* OXAZINE COLOURING MATTERS.

PHENOL AND ITS HOMOLOGUES. When a hydroxyl group enters into the molecule of an aromatic hydrocarbon it can do so by replacing (1) a hydrogen atom of the nucleus or (2) a hydrogen atom of a side chain. The isomeric substances thus produced possess, however, very different properties, for, whereas the compound (2) is in all respects analogous to the aliphatic alcohols, the compound (1) exhibits properties which serve to distinguish it entirely from the members of the aliphatic series.

$$\underset{(1)}{C_6H_4(OH)CH_3} \qquad \underset{(2)}{C_6H_5{\cdot}CH_2(OH)}$$

The members of group (1) are therefore classed by themselves, and since the simplest representative of the series, $C_6H_5{\cdot}OH$, which is produced by the substitution of one hydrogen atom of benzene by hydroxyl, is called phenol, all members of the group are known under the general name of phenols.

Nomenclature. According as one, two, three, four, and so forth, hydroxyl groups enter the benzene nucleus, the phenols are termed monohydric, dihydric, trihydric, tetrahydric phenols respectively. Their scientific names may, in every instance, be referred to the parent hydrocarbon, but in many cases, especially as regards the older members of the series, they are generally known by trivial names which are derived from their mode of origin. Thus 1-3-dihydroxybenzene is termed resorcinol from its similarity to orcinol; 1-2-3-trihydroxybenzene is known as pyrogallol because it was originally prepared by the distillation of gallic acid. The phenols possess the general formula

$$C_nH_{2n-7}(OH) \text{ or } C_nH_{2n-6}O.$$

The Monohydric Phenols. The simplest members of the series frequently occur among the products of the dry distillation of organic compounds containing oxygen, and therefore phenol, and the cresols occur in coal tar. They may be prepared synthetically by the following processes:—

(1) The fusion of a sulphonic acid with potassium hydroxide; thus phenol (potassium salt) is formed from potassium benzene sulphonate in accordance with the equation—

$$C_6H_5{\cdot}SO_3K+2KOH \rightarrow C_6H_5{\cdot}OK+K_2SO_3+H_2O$$

(2) By treating a diazonium salt of an amine with hot water; aniline can be converted into phenol thus—

$$C_6H_5NH_2 \rightarrow C_6H_5N_2Cl+H_2O \rightarrow C_6H_5{\cdot}OH+N_2+HCl$$

The great stability of the halogen derivatives of the aromatic hydrocarbons which have the halogen atoms directly attached to the carbon atoms of the nucleus, prohibits the formation of phenols by the method usually adopted for the preparation of the aliphatic alcohols, namely by the interaction of halogen derivatives of the hydrocarbon and alkaline hydroxides. If, however, a nitro group is present in the aromatic nucleus, the halogen atom, provided that it is in the ortho- or para- position to the negative group, is readily displaced by hydroxyl thus—

$$C_6H_4(NO_2)Br+KOH \rightarrow C_6H_4(NO_2)OH+KBr$$

A nitro group in the meta- position has no effect on the inactivity of the halogen atom.

(3) Phenols may also be prepared by eliminating the carboxyl group from aromatic hydroxy acids.

$$C_6H_4(OH)(CO_2H) \rightarrow C_6H_5(OH)+CO_2$$

General properties. The phenols differ from the aliphatic alcohols in their capacity for forming salts with alkali metals. The corresponding compounds of the aliphatic alcohols, for example sodium ethoxide, are readily and completely dissociated by water, yielding free alkali and the alcohol,

$$C_2H_5{\cdot}ONa+H_2O \rightarrow C_2H_5{\cdot}OH+NaOH$$

whereas a sodium phenolate or phenate $C_6H_5{\cdot}ONa$ dissolves in water without change. The phenols are therefore acid substances which dissolve in aqueous caustic alkalis forming a solution of the salt from which acids reprecipitate the free phenol. The simpler phenols are not, however, acids sufficiently strong to decompose carbonates, but they acquire this property when negative groups are present in the benzene nucleus; thus picric acid dissolves in aqueous alkaline carbonates

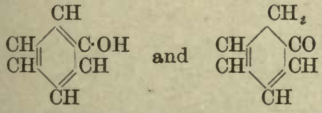
$$2C_6H_2(NO_2)_3OH+Na_2CO_3 \rightarrow 2C_6H_2(NO_2)_3ONa+H_2O+CO_2.$$

The phenols are therefore weak acids and their alkali salts, which are alkaline to litmus, are readily decomposed by carbonic acid. The action of alkyl iodides on the phenolates yields the phenol ethers, of which anisole, $C_6H_5(OCH_3)$, and phenetole, $C_6H_5(OC_2H_5)$, are types

$$C_6H_5{\cdot}ONa+CH_3I \rightarrow C_6H_5{\cdot}OCH_3+NaI$$

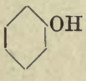
The faintly acid character of phenol is illustrated by the behaviour of these compounds since they are not hydrolysed by alkalis, and are therefore more closely allied in their properties to the ethers than to the ethereal salts. The hydroxyl group in the phenols is readily displaced by hydrogen by distillation with zinc dust and also by the action of phosphorus trisulphide. It is displaced by halogens through the agency of phosphorus pentabromide or chloride, and by the amino group by heating with zinc ammonium chloride or similar salts. The replacement of the hydrogen atoms of the nucleus takes place with remarkable readiness, and the entrance of halogen atoms, as well as of nitroso, nitro, sulphonic acid, and azo groups, into the molecule of the phenols can be effected with great ease.

The phenols are characterised by certain colour reactions which may be ascribed to the tendency they possess to react in the tautomeric forms—

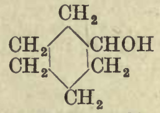


Thus well-defined colourations are usually produced by ferric chloride. Other colour reactions are shown by certain reagents; for example, sulphuric acid containing nitrous acid gives a characteristic colour with many phenols; this reaction is the basis of Liebermann's nitroso reaction. Phenols, having free para positions when fused with phthalic anhydride in the presence of a dehydrating agent, yield phthaleins which dissolve in alkali, forming strongly coloured solutions. The phenols also combine with diazonium salts yielding coloured oxyazo compounds.

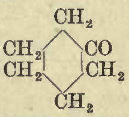
The oxidation of the phenols leads to a variety of products, some produced by the fission of the aromatic ring, as when phenol is converted into oxalic acid by potassium permanganate (Henriques, Ber. 1888, 21, 1619), but more often leading to derivatives of diphenyl by the joining up of two benzene nuclei. The reduction of the phenols could not be effected until Sabatier and Senderens introduced their process of reduction by the aid of nickel at high temperatures. At the present time, practically all the better known phenols have been reduced by this method to the corresponding derivatives of *cyclo*-hexanol. An example may be given in phenol itself which, when its vapour mixed with hydrogen is passed over nickel heated at 215°–230°, is reduced to *cyclo*-hexanol. At the same time, some *cyclo*-hexanone is produced by loss of hydrogen. The mixed product may be either wholly converted into the alcohol by passing it again over nickel at a lower temperature, using a large excess of hydrogen, or into the ketone by conducting the vapour without hydrogen over copper heated at 330° (compare Compt. rend. 1904, 137, 1025; 138, 457, 1257; Brunel, *ibid.* 137, 1268).



(Phenyl.)



(*cycle*-Hexanol.)



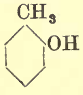
(*cyclo* Hexanone.)

Phenol (**Carbolic acid, hydroxybenzene**). Phenol was discovered by Runge in 1834 (Pogg. Ann. 1834, 31, 69; 32, 308) among the products formed by the distillation of coal tar, and was subsequently obtained in a crystalline condition by Laurent (Annalen, 1842, 43, 200). The preparation of phenol from coal tar is described in the article on carbolic acid (*q.v.*); considerable quantities are made synthetically by the fusion of potassium benzene sulphonate with caustic potash in accordance with the general method already mentioned (1). The purification of phenol can be effected by taking advantage of the formation of a crystalline hydrate of the formula $C_6H_5OH+H_2O$ (m.p. +16°).

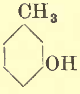
Phenol boils at 183° and solidifies to a mass of large colourless prismatic crystals possessing a characteristic smell. The addition of a small quantity of water to solid phenol causes it to liquefy, since there is formed a solution of water in phenol which is known as 'acidum carbolicum liquefactum.' At the ordinary temperature, about 1 part of water dissolves in 3 parts of phenol. When more water is added an oil separates which ultimately dissolves, yielding a solution of phenol in water; at the ordinary temperature, 1 part of phenol is soluble in 15 parts of water. Phenol is a strong poison, and in its pure condition, or in the form of its concentrated solution, quickly corrodes the skin. It is a powerful aseptic and is employed for this purpose in the form of a 3 p.c. aqueous solution. Phenol is used technically for a variety of purposes; thus it is employed in the preparation of salicylic acid and phenacetin, as well as for the production of picric acid (*q.v.*); it is also the basis of many colouring matters. The presence of phenol (in the absence of other members of the series) may be detected by the violet colour which is produced by ferric chloride, but a more delicate test is to add bromine water to an aqueous solution of the substance, when even in very dilute solution a flocculent pale yellow precipitate of tribromphenol, $C_6H_2Br_3(OH)$, mixed with tribromphenol bromide, $C_6H_2Br_3{\cdot}OBr$, is at once formed.

The esters of phenol. Phenyl hydrogen sulphate, $C_6H_5{\cdot}O{\cdot}SO_2OH$. is formed as the potassium salt when a concentrated solution of potassium phenolate is treated with potassium pyrosulphate. The salt crystallises from alcohol in small glistening leaflets which dissolve in 7 parts of water at 15°. It is stable towards alkalis but is at once decomposed by acids into phenol and acid potassium sulphate. The free acid is unstable both in alcoholic and in aqueous solution. Potassium phenyl sulphate is of some physiological importance since it is in this form that phenol, taken internally, is excreted. It occurs in small quantity in the normal urine of men and dogs. *Phenol methyl ether* (anisole *q.v.*) $C_6H_5{\cdot}OCH_3$. is a pleasant-smelling liquid boiling at 153·9° and melting at −37·8°. It has sp.gr. 0·990 at 22°. *Phenol ethyl ether* (phenetole), $C_6H_5-OC_2H_5$, boils at 170·3° and has sp.gr. 0·969 at 16°.

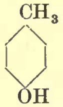
The Cresols. The entrance of a hydroxyl group into the molecule of the hydrocarbon toluene can take place either in the side chain or in the aromatic nucleus. In the former event the compound produced is, as already mentioned, aliphatic in character and need not be considered here. It is only when the hydroxyl group enters the aromatic nucleus that the cresols are formed. It is evident that the hydroxyl group can enter in three positions in respect to the methyl group, and hence there are three cresols which may be represented by the formulæ



ortho-Cresol.



meta-Cresol.

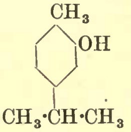


para-Cresol.

All three cresols occur in coal tar in relatively large quantities, although *o*-cresol is the only member which is isolated, commercially, in a pure condition. Both *o*- and *p*-cresol are prepared in a pure state from the corresponding toluidines through the diazo reaction (method 2). *m*-Cresol is usually derived from thymol by heating it with phosphorus pentoxide. o-*Cresol* (1-methyl-2-hydroxybenzene) melts at 30° and boils at 190·8°. m-*Cresol* (1-methyl-3-hydroxybenzene), melts at 4° and boils at 202·8°. p-*Cresol* (1-methyl-4-hydroxybenzene), melts at 36° and boils at 201·8° (*v.* Cresol).

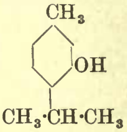
The six possible *xylenols* (dimethylhydroxybenzenes) have been prepared either from the corresponding xylidines or from the isomeric xylene sulphonic acids by fusion with potash: *adj-o-xylenol* (1:2-dimethyl-3-hydroxybenzene), melts at 73° and boils at 213°; *asym-o-xylenol* (1:2-dimethyl-4-hydroxybenzene), melts at 65° and boils at 222°; *adj-m-xylenol* (1:3-dimethyl-2-hydroxybenzene), melts at 49°; *asym-m-xylenol* (1:3-dimethyl-4-hydroxybenzene), melts at 25° and boils at 209°; *sym-m-xylenol* (1:3-dimethyl-5-hydroxybenzene), melts at 63° and boils at 218°; *p-xylenol* (1:4-dimethyl-2-hydroxybenzene), melts at 75° and boils at 209°. The three more important trimethylhydroxybenzenes are: *mesitol* (1:3:5-trimethyl-2-hydroxybenzene), melting at 70°–71° and boiling at 219·5°; *pseudocumenol* (1:2:4-trimethyl-5-hydroxybenzene), which melts at 73° and boils at 234°–235°, and *hemellithenol* (1:2:3-trimethyl-5-hydroxybenzene), melting at 81°. *Prehnitenol* is 1:2:3:4-tetramethyl-5-hydroxybenzene; it melts at 86°–87° and boils at 266°. *Durenol*, which is 1:2:4:5-tetramethyl-3-hydroxybenzene, melts at 117° and boils at 249°–250°.

Two important substances are included among the higher phenols, namely *carvacrol* and *thymol*. These compounds occur naturally in many ethereal oils and are related to the terpenes and camphors. They are both monohydric phenols derived from cymene (1-methyl-4-*iso*propylbenzene), and since this hydrocarbon can only yield two phenols, namely



I.

and

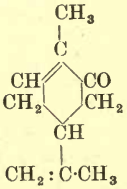


II.

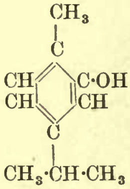
it is evident that one must be thymol and the other carvacrol.

The structure of the two compounds is revealed by the fact that when heated with phosphorus pentoxide, carvacrol yields propylene and *o*-cresol; its constitution is therefore represented by formula (I.). Thymol, on the other hand, yields propylene and *m*-cresol under the same conditions and must therefore have the structure represented by formula (II.).

Carvacrol (1-methyl-4-*iso*propyl-2-hydroxybenzene), occurs in the ethereal oils of *Origanum hirtum* and *Satureja hortensis*, and also in small quantity in the oil of *Thymus serpyllum*. It may be prepared synthetically by fusing sodium cymene sulphonate with caustic soda and can be extracted from the acidified product by means of ether. It is readily formed from its isomeride carvone, a constituent of cumin oil, either by heating with caustic potash or by the action of phosphoric acid. The relation between these substances is shown by the following formulæ—



Carvone.



Carvacrol.

It is also derived from camphor by the action of iodine. Carvacrol is a thick liquid which boils at 237°; it solidifies when cooled and melts at +0·5°. It gives a green colouration with ferric chloride in dilute alcoholic solution.

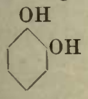
Thymol (1-methyl-4-*iso*propyl-3-hydroxybenzene), occurs in the essential oils of the common garden thyme, *Thymus vulgaris*; of *Ptychotis ajowan*; and of horsemint, *Monarda punctata*, as well as in the essential oil of *Thymus serpyllium*. It may be obtained by shaking oil of thyme with aqueous caustic soda, separating the undissolved terpenes, and acidifying the alkaline extract with hydrochloric acid. The precipitated thymol is then recrystallised from acetic acid.

Thymol forms large transparent crystals, soluble in 1100 parts of water at 16°. It is readily volatile with steam, but the aqueous solution is not coloured by ferric chloride. It melts at 50° and boils at 232°. It is a valuable aseptic and can, since it is less poisonous than phenol, be taken internally. When an aqueous solution of thymol is treated with a half part of acetic acid and then with one part of sulphuric acid and warmed, a red-violet colour is produced.

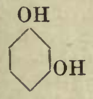
A reaction by which certain higher monohydric phenols can be produced has been introduced by Liebermann (Ber. 1881, 14, 1842). It is carried out by treating aliphatic alcohols with phenol in the presence of zinc chloride. Thus p-*isobutylphenol* (4-*iso*butyl-1-hydroxybenzene) can be prepared by heating phenol (10 parts), *iso*butyl alcohol (8 parts), and zinc chloride (24 parts) at 180°. It crystallises in needles, melts at 97·4°–98° and boils at 236°–238°. A similar reaction has been discovered by Königs (Ber. 1890, 23, 3145), only in this case the olefinic hydrocarbons are treated with phenol in the presence of a mixture of one part concentrated sulphuric acid and nine parts of glacial acetic acid. The two reactions may be represented by the equations—

(1) $C_4H_9(OH)+C_6H_5{\cdot}OH \rightarrow C_4H_9{\cdot}C_6H_4{\cdot}OH+H_2O.$
(2) $C_5H_{10}+C_6H_5{\cdot}OH \rightarrow C_5H_{11}{\cdot}C_6H_4{\cdot}OH.$

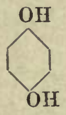
The dihydric phenols. The formula of benzene permits of the existence of three isomeric dihydroxy derivatives; their names and formulæ are given below



1:2-Dihydroxybenzene (pyrocatechol).



1:3-Dihydroxybenzene (resorcinol).



1:4-Dihydroxybenzene (hydroquinone).

As products of the decomposition of naturally occurring substances, these dihydric phenols have been known from the earliest times; their orientation was first suggested by Petersen (Ber. 1873, 6, 308; 1874, 7, 58).

Pyrocatechol (1:2-dihydroxybenzene), was first obtained by Reinsch in 1839 (Ber. 20, 301) by the dry distillation of catechin (*Mimosa catechu*). It is obtained by the distillation of catechins and is frequently prepared by the distillation of those vegetable substances which give a green colouration with ferric salts (Wagner, Annalen, 1850, 76, 351; Uloth, *ibid.* 1859, 111, 215). It is, moreover, formed in the distillation of wood and is therefore present in crude pyroligneous acid.

Preparation. (1) Pyrocatechol can be made from its methyl ether, *guaiacol*, which is the chief constituent of the fraction of beech wood tar which boils at 200°–205°. The hydrolysis can be effected and a yield of 70 p.c. obtained by the following process (Hartmann and Gattermann, Ber. 1892, 25, 3532). 15 grms. of guaiacol, cooled from without by ice, are gradually mixed with 12 grms. of aluminium chloride and then heated in an oil bath for 2 hours at 210°. At the end of this time the product, which is a hard solid cake, is removed from the flask, ground to powder and warmed with dilute hydrochloric acid, by which process the soluble pyrocatechol is removed from unchanged guaiacol and resinous products. The aqueous extract is then saturated with common salt and the phenol extracted by ether. Pyrocatechol remains on evaporating the solvent and is purified by distillation.

According to Perkin (Chem. Soc. Trans. 1890, 57, 587), an almost quantitative yield of pyrocatechol can be obtained from guaiacol by the following means. A solution of guaiacol in 1·5 times its weight of fuming hydriodic acid (sp.gr. 1·96) is gently heated for about an hour in an apparatus fitted with a reflux condenser (to condense the eliminated methyl iodide), allowed to cool, mixed with a fourth of its weight of hydriodic acid and heated as before for 1 hour. The product, after washing with water, is extracted by ether, the ether removed by distillation and the residual oil purified by rapid fractionation.

(2) Pyrocatechol may be obtained in a pure condition by fusing phenol-*o*-sulphonic acid with 24 molecular proportions of caustic potash at 320°–330°; the yield is 20 p.c. of the theoretical. By using less potash or a lower temperature a smaller yield is obtained.

Pyrocatechol crystallises from benzene as glistening colourless plates which melt at 104°; it boils at 240° and is slowly volatile with steam. 31·1 parts are soluble in 100 parts of water at 20°, and the aqueous solution gives a green colouration with ferric chloride, which changes to violet on the addition of sodium carbonate or acetate; this reaction is characteristic of the ortho-dihydroxy derivatives of benzene. The aqueous solution gives a white precipitate with lead acetate, and the formation of this salt, which is insoluble in water, is used for the quantitative estimation of the phenol. The salt can be dried at 100°–110°, and has the composition $C_6H_4O_2Pb$.

Derivatives of pyrocatechol. The ethers of pyrocatechol are of considerable importance, and many natural products are derivatives of the methyl ethers and especially of the methylene ether (*v.* PIPERONAL).

Guaiacol $OH{\cdot}C_6H_4{\cdot}OCH_3$, was originally prepared by the distillation of guaiacum resin (Unverdorben, Pogg. Ann. 1826, 8, 402), and is also obtained in large quantities by the distillation of wood. It is best derived from the fraction of beechwood tar, boiling at 200°–220° by the following process (Hlasiwetz, Annalen, 1858, 106, 339). The fraction is repeatedly shaken with moderately strong ammonia, then washed with water and rectified. The product is then dissolved in an equal volume of ether, and the potassium salt, which separates on the addition of a slight excess of alcoholic potash, is washed with ether, recrystallised from alcohol, and finally decomposed by dilute sulphuric acid. Guaiacol may be obtained synthetically by direct methylation, for which purpose molecular quantities of pyrocatechol, caustic potash, and potassium methyl sulphate are heated at 170°–

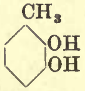
180° (Gorup, Annalen, 1868, 147, 248; Béhal and Choay, Bull. Soc. chim. 1893, [iii.] 9, 142).

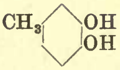
The barium salts of guaiacol and creosol (the mono-methyl ether of homo-catechol, 3:4-dihydroxy-1-methylbenzene) are much less soluble in water than those of the admixed phenols, and a process for the separation of these substances, depending on this property, has been applied technically (D. R. P. 56003, 90). Beechwood tar (40 kilos.), is mixed with barium hydroxide (64 kilos.) and 150 litres of hot water. On cooling, the crystalline magma is filtered off, pressed, washed once with water, and the guaiacol, which is mixed with more or less creosol, separated by the addition of hydrochloric acid and subsequently steam distilled. The distillate, on treatment with aqueous potash, gives the sparingly soluble salts of guaiacol and creosol, the two phenols being finally separated by distillation.

Guaiacol has only within comparatively recent times been obtained in a chemically pure condition (Béhal and Choay, Bull. Soc. chim. 1893, [iii.] 9, 142). It melts at 28·5° and boils at 205°, dissolves in 60 volumes of water at 15°, and has sp.gr. 1·143 at 15°. A 1 p.c. solution in alcohol gives a blue colouration with ferric chloride, changing quickly through green to yellow. When heated with phosphorus pentachloride it is converted into *o*-chloranisole; a reaction by which its relationship with pyrocatechol and its orientation was originally determined (Fishli, Ber. 1878, 11, 1461).

Veratrole $C_6H_4(OCH_3)_2$, (pyrocatechol dimethyl ether, 1:2-dimethoxybenzene) is obtained by the distillation of veratric acid with baryta and also by the methylation of the potassium salt of guaiacol. It melts at 22·5°, boils at 205°, and has sp.gr. 1·081 at 21·2°.

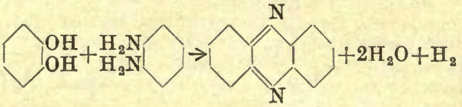
Other ortho-dihydric phenols. Two methyl derivatives can be derived from pyrocatechol by the entrance of a methyl group into the benzene ring, namely



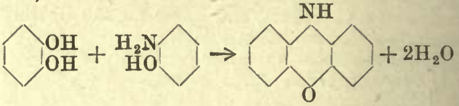


The first is *isohomopyrocatechol*, 2:3-dihydroxy-1-methylbenzene, which melts at 47° and boils, with partial decomposition, at 238°–240°. The second is *homocatechol*, 3:4-dihydroxy-1-methylbenzene, melting at 51° and boiling at 251°–252°. The methyl ether of this substance, *creosol* (4-hydroxy-3-methoxy-1-methylbenzene), accompanies guaiacol as a constituent of beechwood tar; it boils at 221°–222° and has sp.gr. 1·111 at 0°.

Reactions of ortho-dihydric phenols. Apart from the special reactions already mentioned, the ortho-dihydroxy derivatives of benzene are characterised by the following properties. When treated with *o*-phenylenediamine they yield phenazines or derivatives of this substance. Thus pyrocatechol gives phenazine (Ris, Ber. 1886, 19, 2206). With *o*-aminophenols they yield phenoxazines, as is illustrated by the formation of phenoxazine from pyrocatechol and *o*-aminophenol (Bernthsen, *ibid.* 1887, 20, 942)



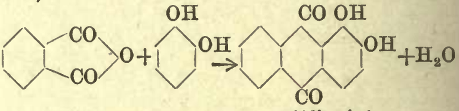
(Phenazine.)



(Phenoxazine.)

They also yield thiodiphenylamines when treated with *o*-aminothio phenols (Bernthsen, *ibid.* 1887, 19, 3255).

Other typical condensations may be illustrated by the formation of alizarin from phthalic anhydride and pyrocatechol with sulphuric acid (Baeyer and Caro, Ber. 1876, 7, 972)—



(Alizarin.)

and by the production of a phthalein from pyrocatechol and phthalic anhydride in the presence of zinc chloride at 140° (Baeyer and Kochendörfer, Ber. 1889, 22, 2196).

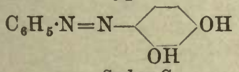
Resorcinol $C_6H_4(OH)_2$ (Resorcin, 1:3-dihydroxybenzene) was first obtained by Hlasiwetz and Barth (Annalen, 1864, 130, 354) by melting certain resins (galbanum, &c.) with potash. It is probable that all resins which yield umbelliferone on dry distillation react in this manner (*cf. ibid.* 1866, 139, 83, 100). Resorcinol can also be obtained from benzene-disulphonic acids, halogensulphonic acids and halogenphenols; it is prepared on the technical scale from sodium benzene-*m*-disulphonate by fusion with caustic soda (Mühlhaüser, Dingl. poly. J. 1887, 263, 154). The preparation from benzene is thus described by Bindschedler and Busch (Mon. Sci. 1878, 1169; J. 1878, 1137). To prepare benzene-*m*-disulphonic acid, 90 kilos. of fuming sulphuric acid are placed in a cast-iron vessel provided with a stirring apparatus, and attached to a reflux condenser, and 24 kilos. of pure benzene are gradually run in with constant stirring; the temperature gradually rises to the boiling-point of benzene, and in the course of two to three hours the benzene is completely converted into the mono-sulphonic acid. The reflux condenser is then removed, the vessel attached to a condenser arranged in the ordinary way, and the temperature raised to 275° in order to convert the mono-sulphonic acid into the disulphonic acid. Any benzene which comes off with the water formed at this stage of the reaction is collected in the receiver. After heating for about 20 minutes at this temperature, the mass is allowed to cool, then poured into 2000 litres of water, neutralised with milk of lime, and converted into the sodium salt in the usual way, the solution of the salt being subsequently evaporated to dryness. To obtain resorcinol from this product, 60 kilos. of the completely dry sodium salt are added to 150 kilos. of caustic soda dissolved in the smallest possible quantity of water, and the mass heated at 270°

in a cast-iron vessel with continual stirring for from 8 to 9 hours, during which time it becomes gradually semi-solid and finally solid. On cooling, it is dissolved in 500 litres of boiling water, the solution acidified with hydrochloric or sulphuric acids and boiled until all sulphur dioxide has escaped. The tarry matter, which is deposited, is filtered off from the cold solution, and the filtrate thoroughly extracted with ether in a copper extraction apparatus, the ether being subsequently distilled off and recovered. The crude resorcinol, obtained in this manner, is a colourless crystalline mass, which can be freed from traces of ether and water by heating it in an enamelled vessel at 215°. It then forms a hard brittle mass containing 92–94 p.c. of resorcinol together with some phenol and about 5 p.c. of tarry matter. To free it from these impurities it is distilled, water coming over first, then phenol and finally resorcinol. It can be further purified by sublimation or recrystallisation from benzene. Resorcinol may also be prepared from *m*-aminophenol through the diazo compound (Bantlin, Ber. 1878, 11, 2101).

Resorcinol crystallises from benzene in large colourless needles which melt at 119°; it boils at 276·5°, and is slowly volatile with steam: 100 parts of resorcinol dissolve in 67·9 parts of water at 12·5°. The aqueous solution gives a dark violet colour with ferric chloride which is discharged on the addition of sodium acetate. It gives no precipitate with lead acetate and can, by this means, be distinguished from pyrocatechol. Resorcinol gives a voluminous precipitate of tribromresorcinol with bromine water and reduces both ammoniacal silver nitrate solution and Fehling's solution when warmed. On fusion with potash it is converted into a mixture of phloroglucinol (60–70 p.c.), pyrocatechol (2–3 p.c.) and diresorcinol (1·5 p.c.) (Barth and Schreder, Ber. 1881, 12, 503).

When fused with phthalic anhydride, resorcinol is converted into fluorescein and the presence of small quantities can be detected by means of this reaction. The test is best effected by dissolving the substance in dilute ammonia and pouring the solution into a large volume of water, when the presence of resorcinol is indicated by the formation of a yellow solution having a fine green fluorescence.

Resorcinol and its analogues (the aminophenols, &c.) are extensively used in the preparation of colouring matters (*see* PYRONINE COLOURING MATTERS). It combines with diazonium salts forming oxyazo colouring matters of which Sudan G is a type



Sudan G.

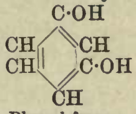
but these compounds have little technical importance.

Resorcinol may be estimated quantitatively by titration with bromine water or by means of a solution of bromine in alkali, as in the case of phenol. The method is based on the formation of tribromresorcinol in accordance with the equation

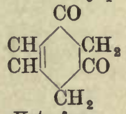
$$C_6H_4(OH)_2+3Br_2 \rightarrow C_6HBr_3(OH)_2+3HBr$$

Delicate tests for resorcinol are described by Carobbio (Chem. Zentr. 1906, [ii.] 632) and by Silbermann and Ozorovitz (*ibid.* 1908, [ii.] 1022).

General properties of the meta-dihydric phenols. The tendency for the phenols to react in the keto (hydroaromatic) form increases with the entrance of hydroxyl groups in the meta-position. This tendency is therefore exhibited to a greater extent by resorcinol than by phenol



Phenol-form.

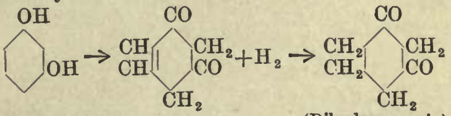


Keto-form.

and is shown to a much greater degree by phloroglucin (*q.v.*).

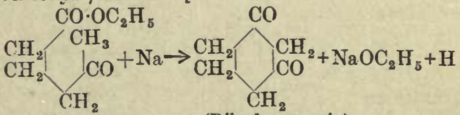
Although the keto form of resorcinol is not sufficiently stable to cause this substance to react with the usual ketonic reagents (hydroxylamine, &c.), yet there is no doubt that the formation of C-alkyl derivatives by the action of alkyl iodides on the sodium salt of resorcinol (*cf.* Herzig and Zeisel, Monatsh. 1889, 12, 191, 368; Ciamician and Silber, Gazz. chim. ital. 1893, 22, 2, 56) is due to the phenol reacting in its keto form.

It has, moreover, been found by Merling (Annalen, 1893, 278, 20) that, unlike phenol, resorcinol is readily reduced by sodium amalgam to dihydroresorcin



(Dihydroresorcin).

a typical alicyclic diketone which has been prepared by Vorländer (Ber. 1897, 28, 2348; Annalen, 1897, 294, 269) by the action of sodium on ethyl-γ-acetobutyrate



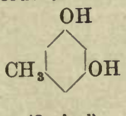
(Dihydroresorcin).

The meta-dihydric phenols also react with aqueous alkaline bicarbonates, yielding the salts of hydroxy acids thus—

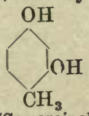
$$C_6H_4(OH)_2+KHCO_3 \rightarrow C_6H_3(OH)_2·COOK+H_2O$$

(*v.* Kostanecki, Ber. 1885, 18, 3202).

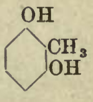
Homologues of resorcinol. There are three possible dihydroxytoluenes which can be formed by the entrance of a methyl group into the nucleus of resorcinol, namely—



(Orcinol)
I.



(Cresorcinol)
II.



III.

Orcinol (3:5-dihydroxy-1-methylbenzene) was discovered by Robiquet in 1829, and is found in many lichens (*Rocella tinctoria*, *Lecanora*, &c.). It is formed by the elimination of carbon dioxide from orsellinic acid, *e.g.* upon fusing extract of aloes with potash—

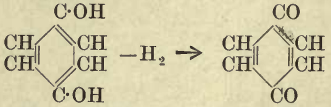
$$C_6H_2(CH_3)(OH)_2COOH \rightarrow C_6H_3(CH_3)(OH)_2+CO_2$$

(Orcinol).

and can also be prepared synthetically from toluene (Ber. 1882, 15, 2992). It is also formed by the action of sodium on ethyl acetouedicarboxylate (*ibid.* 1886, 19, 1446).

Orcinol crystallises from water in prisms containing water of crystallisation which begin to melt at about 56° in their hydrated state; when anhydrous it melts at 107°–108°. It gives a violet-black colouration with ferric chloride, but does not yield a phthalein when fused with phthalic anhydride. Its alkaline solution, when warmed with chloroform, gives a bright-red liquid which shows a strong yellowish-green fluorescence on dilution (homofluorescein reaction). *Cresorcinol* (2:4-dihydroxy-1-methylbenzene, formula II.), melts at 102°–104° and boils at 267°–270°; 2:6-*dihydroxy*-1-*methylbenzene*, formula III., melts at 63°–66°. Both the above compounds give the fluorescein reaction. p-*Xylorcinol* (β-orcinol, 3:5-dihydroxy-1:4-dimethylbenzene), is formed by the decomposition of barbatic acid; it melts at 163° and boils at 277°–280°.

Hydroquinone $C_6H_4(OH)_2$, (Quinol, 1:4-dihydroxybenzene). The para-dihydroxy derivatives of benzene possess the property of readily loosing two atoms of hydrogen in the presence of oxidising agents and passing into quinones (*q.v.*)—



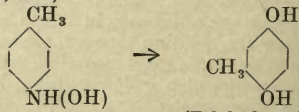
Hydroquinone. Quinone.

They are therefore named hydroquinones. Hydroquinone was first prepared by Caventou and Pelletier from quinic acid on dry distillation, and was further investigated by Wöhler (Annalen, 1844, 51, 145). It occurs naturally in the sugar-bush (*Protea mellifera*), a shrub of common occurrence in South Africa (Hesse, *ibid.* 1896, 290, 317). It can be obtained synthetically by a number of processes, of which the following are the more important. From phenol by oxidation with alkaline potassium persulphate (D. R. P. 81068, 1895; Chem. Fabrik. vorm. E. Schering); by fusing *p*-iodophenol with potash (Körner, Zeitsch. physical. Chem. 1866, 662, 731); and from *p*-diazophenol sulphate when boiled with 10–15 p.c. sulphuric acid (Weselsky and Schuler, Ber. 1876, 9, 1159). It is also formed when the glucoside arbutin is hydrolysed by boiling dilute sulphuric acid (Kawalier, Annalen, 1852, 84, 358; Strecker, *ibid.* 1858, 107, 228) and is produced by the electrolytic oxidation of benzene in alcohol-sulphuric acid solution (Gattermann and Friedrichs, Ber. 1894, 27, 1942). It has been prepared from ethyl succinate through ethyl succinosuccinate (Hermann, Annalen, 211, 336).

The *preparation* of hydroquinone is best effected by the oxidation of aniline in the following way. A concentrated aqueous solution of sodium dichromate is gradually added to a well-cooled (5–10 p.c.) solution of 1 part of aniline in 8 parts of sulphuric acid and 25 parts of water. The mixture at first becomes green, and towards the end of the operation, deep blue-black; a further addition of the dichromate solution brings about the solution of the greater part of the precipitate, and a brown, turbid liquid is obtained containing quinone and quinhydrone in suspension. The quinone and quinhydrone are then reduced to hydroquinone by passing sulphur dioxide through the liquid until it smells of sulphurous acid, the suspended matter is filtered off, and the hydroquinone extracted from the filtrate by means of ether, which is subsequently distilled off. The yield of crude hydroquinone under these conditions amounts to as much as 85 p.c. In order to purify the product it is dissolved in the smallest possible amount of water, the solution boiled with animal charcoal and a little sulphurous acid, filtered and allowed to crystallise.

Hydroquinone is dimorphous. It crystallises from water in colourless hexagonal prisms which, on heating, sublime in monoclinic scales. It melts at 169°–170° and boils at 285° (730 mm.); 100 parts of a solution of hydroquinone saturated at 15° contain 5·85 parts of the phenol and it is readily soluble in alcohol, ether, and in hot water. Ferric chloride converts it into quinone and quinhydrone, and an aqueous solution gives no precipitate with lead acetate. Its alkaline solution becomes brown on exposure to the air. It reduces Fehling's solution in the cold and ammoniacal silver nitrate solution on warming, owing to the formation of quinone, and this oxidation to quinone is effected by nitric acid, chlorine or other oxidising agents. When its vapour is passed through a tube heated to redness, it is transformed into quinone and free hydrogen (Hesse, Annalen, 1860, 114, 297). When heated with phthalic anhydride and sulphuric acid it yields quinazarin, and when heated with phthalic anhydride and zinc chloride it is converted into the colourless hydroquinonephthalein (Grimm, Ber. 1873, 6. 506).

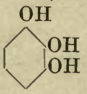
Homologues of hydroquinone are usually named after the parent hydrocarbon. *Toluhydroquinone*, $C_6H_3(CH_3)(OH)_2$ (2:5-dihydroxy-1-methylbenzene), is of interest because it is formed by the action of hot dilute sulphuric acid on *p*-tolylhydroxylamine (Bamberger, Ber. 1895, 28, 246)—



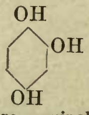
(Toluhydroquinone.)

It melts at 125°. Of the *xylohydroquinones*, the *ortho*- compound melts at 221°, the *meta*- compound at 149°, and the *para*- derivative at 211°.

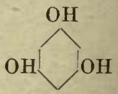
The trihydric phenols. The three theoretically possible trihydroxy derivatives of benzene are known; they are



(Pyrogallol.)



(Hydroxyquinol.)



(Phloroglucinol.)

Pyrogallol, $C_6H_3(OH)_3$ (pyrogallic acid, 1:2:3-trihydroxybenzene), was first prepared by Scheele in 1786 by the dry distillation of gallic acid—

$$\underset{\text{(Gallic acid.)}}{C_6H_2(OH)_3COOH} \rightarrow C_6H_3(OH)_3+CO_2$$

and it is by this process that it is prepared commercially at the present day. It is also formed from α- or β-parachlorophenolsulphonic acid by fusion with potash (Petersen and Baehr-Predari, Annalen, 1871, 157, 136). The *preparation* of pyrogallol is usually carried out as follows. Gallic acid is heated with 2–3 times its weight of water in a bronze digester at 200°–210° for about half an hour, the escape of carbon dioxide evolved during the operation being provided for. The resulting almost colourless solution of pyrogallol is then boiled with animal charcoal, filtered, the filtrate rapidly evaporated, and the pyrogallol, which crystallises out, distilled under a pressure of 20–30 mm. The yield is practically theoretical.

In order to obtain the phenol cheaply for photographic purposes, T. E. Thorpe (Chem. News, 43, 109) recommends that 10 grms. of gallic acid and 30 grms. of glycerol be heated at 190°–200° as long as carbon dioxide is evolved. A theoretical yield is obtained and the mass dissolved in a litre of water, gives a solution suitable for photographic work. For the preparation of pyrogallol from 2 : 6-dihalogen-1-phenol-4 sulphonic acids, *cf.* D. R. P. 207374, 1907.

Pyrogallol forms white lustrous needles or thin plates, melts at 132° and boils with partial decomposition at 210°. It is soluble in 2·25 parts of water at 13°, has a bitter taste and is poisonous. It is readily soluble in ether and in alcohol and its alkaline aqueous solution absorbs oxygen from the air, becoming deep-brown in colour. It is upon this property that the employment of an alkaline solution of pyrogallol in gas analysis depends. The absorption of oxygen involves the decomposition of the phenol into carbon dioxide, acetic acid, carbon monoxide and products of high molecular weight; allowance must be made for the production of the small quantity of carbon monoxide formed in this manner (see below). Gold, silver, and mercury salts are rapidly reduced by pyrogallol; a solution of a ferrous salt, free from any trace of ferric salt, produces a white turbidity when added to a solution of pyrogallol, but if any ferric salt be present, a blue colouration is at once formed, which rapidly changes to a brown-red, owing to the oxidation of the pyrogallol by the ferric salt to a product giving a blue colour with ferrous salts (Jacquemin, Compt. rend. 1873, 77, 593). Ferric salts in excess and other oxidising agents, such as potassium permanganate and chromic acid, oxidise pyrogallol to purpurogallin (Wichelhaus, Ber. 1872, 5, 848), a red compound which yields naphthalene on distillation with zinc dust. When heated with phthalic anhydride, pyrogallol is converted into gallein (*q.v.*); it is usual to employ gallic acid in the preparation of this substance since at the high temperature of the reaction it is converted into pyrogallol. Anthragallol is formed when this condensation is effected in the presence of a condensing agent such as excess of strong sulphuric acid (Seuberlich, Ber. 1877, 10, 42).

The employment of pyrogallol in gas analysis. It has been found that 1 grm. of pyrogallol, dissolved in aqueous potash, is capable of absorbing 189·8 c.c. of oxygen (Liebig, Annalen, 77, 107). Oxygen is most rapidly absorbed by a solution of either 0·25 grms. of pyrogallol in 10 c.c. of aqueous potash of sp.gr. 1·050 (Weyl and Zeitler, Annalen, 1880, 205, 255), or by the same amount of the phenol in 10 c.c. of aqueous caustic soda of sp.gr. 1·030 (Weyl and Goth, Ber. 1881, 14, 2659). The amount of carbon monoxide evolved is greater with pure oxygen than with a mixture of oxygen and nitrogen, being about 3·5 p.c. with pure oxygen, and 2·5 p.c. with air, of the quantity of oxygen absorbed (Calvert, Cloez and Bousingault, Compt. rend. 57, 873: Annalen, 1864, 130, 248).

The ethers of pyrogallol. The dimethyl ether (pyrogallol dimethyl ether),

$$C_6H_3(OH)(OCH_3)_2, (OH : OCH_3 : OCH_3 = 1 : 2 : 3),$$

occurs in beechwood tar creosote, and can be isolated by treating the fraction boiling at 250°–270° with benzoyl chloride, and subsequently decomposing the crystalline benzoyl derivative (m.p. 118°) with alkali (Hofmann, Ber. 1875, 8, 66; 1878, 11, 329; 1879, 12, 1371). It forms white prisms, melts at 52° and boils at 253°. When oxidised with nitric acid, ferric chloride, chlorine, or preferably chromic acid in acetic acid solution, it yields cedriret.

The isomeric dimethyl ether

$$(OH : OCH_3 : OCH_3 = 2 : 1 : 3),$$

has been prepared by Graebe and Hesse (Annalen, 1905, 340, 232) by heating syringic acid at 240°–270°; it melts at 54·8° and boils at 262·7°. It is converted into cedriret when oxidised with sodium nitrite in acid solution.

Hydroxyquinol, $C_6H_3(OH)_3$ (1 : 3 : 4-trihydroxybenzene), is obtained together with diquinol and δ-hexahydroxydiphenyl, by very rapidly heating hydroquinone with 8–10 times its weight of caustic soda until the evolution of hydrogen has almost ceased (Barth and Schreder, Monatsh. 1883, 4, 176; Herzig and Zeisel, *ibid.* 1888, 9, 149). It crystallises from ether in microscopic scales, melts at 140·5° and distils with partial decomposition into quinol. Its aqueous solution becomes rapidly coloured on exposure to the air, and when treated with a drop or two of aqueous ferric chloride gives a transient bluish-green colouration, which, on the addition of a very small quantity of aqueous sodium carbonate, becomes dark-blue and on the addition of a further amount, wine-red. For an account of the derivatives of oxyhydroquinone, compare Bargellini and Avrutin (Chem. Zentr. 1911, [i.] 216, 217). The *trimethyl derivative* 1 : 2 : 4-trimethoxybenzene, boils at 247° and is prepared by the action of dimethylsulphate on oxyhydroquinone triacetate (Schuler, Arch. Pharm. 1907, 245, 262). It has been used by Reigrodski and Tambor (Ber. 1910, 43, 1964) for the synthesis of 2 : 3-dioxyflavone.

Phloroglucinol, $C_6H_3(OH)_3$ (1 : 3 : 5-trihydroxybenzene), is obtained by fusing with potash certain glucosides, as for example phloretin, whence its name (Hlasiwetz, Annalen, 1855, 96, 120), quercitrin obtained from species of *Quercus* (Hlasiwetz, *ibid.* 1859, 112, 98), maclurin, which, in an impure form, is obtained from fustic (Hlasiwetz and Pfaundler, *ibid.* 1863, 127, 357), catechin, kino (Hlasiwetz, *ibid.* 134, 118), dragon's blood (Hlasiwetz and Barth, *ibid.* 1865, 134, 283), gamboge (Hlasiwetz and Barth, *ibid.* 1866, 138, 69), and scoparin, a yellow dye obtained from *Spartium scoparum* (Hlasiwetz, *ibid.* 1866, 138, 190). It is also obtained by fusing benzene trisulphonic acid, phenol (Barth and Schreder, Ber. 1879, 12, 422), resorcinol (Barth and Schreder, *ibid.* 1879, 12, 503), or orcinol (Barth and Schreder, Monatsh, 1882, 3, 649) with an excess of caustic soda. It has been prepared synthetically from ethyl malonate by Baeyer (Ber. 1885, 18, 3458); compare also Moore (Chem. Soc. Trans. 1904, 85, 165).

Preparation. It is best prepared by fusing resorcinol for about 25 minutes with 6 parts of caustic soda at a gradually increasing temperature until the vigorous evolution of gas, which soon sets in, almost ceases and the mass becomes a bright chocolate colour. The mass is then dissolved in water and the solution acidified with dilute hydrochloric acid, filtered, and extracted with ether; the ether being subsequently distilled off, and the phloroglucinol, which separates as a magma, recrystallised after purification with animal charcoal (Barth and Schreder, *l.c.*).

The product usually contains some resorcinol, which can be removed by heating at 100° and moistening with water from time to time until all the resorcinol has been sublimed (Tiemann and Will, Ber. 1881, 14, 954).

Phloroglucinol can be completely freed from resorcinol and diresorcin by boiling with a concentrated aqueous solution of potassium bicarbonate. Under these circumstances, the potassium salt of phloroglucinolcarboxylic acid is formed which crystallises in needles, is sparingly soluble in a solution of potassium carbonate and alcohol, and when added to dilute hydrochloric acid gives the free acid which can be extracted with ether. The crystalline acid obtained by evaporating the ether solution eliminates carbon dioxide when boiled with water, pure phloroglucinol remaining in the solution (Will and Albrecht, Ber. 1884, 17, 2103; Will, *ibid.* 1885, 18, 1323; Skraup, Monatsh. 1889, 10, 721).

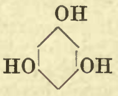
According to Brunner (Annalen, 1907, 351, 313), potassium phloroglucinolcarboxylate is formed at the ordinary temperature when a stream of carbon dioxide is passed through a mixture of the phenol and potassium carbonate in glycerol.

Phloroglucinol crystallises from water in colourless tables containing $2H_2O$, and from ether in large rhombic plates. These lose their water of crystallisation at 100°, forming the anhydrous compound which melts at 217°–219° when rapidly heated, but at 200°–209° when slowly heated (Baeyer, Ber. 1886, 19, 2186). It sublimes without decomposition, has a sweet taste, reduces Fehling's solution, is readily soluble in water, alcohol, and in ether, and, according to Tiemann and Will (*l.c.*), is more readily extracted from a neutral than from an acid solution. It is a dibasic acid (Thiele and Roemer, Zeitsch. physikal. Chem. 1908, 63, 711) and its alkaline solution absorbs oxygen from the air, but less readily than pyrogallol (Weyl and Goth, Ber. 1881, 14, 2673). Its aqueous (concentrated) solution gives a blue-violet colour with ferric chloride.

When potassium nitrate is added to a very dilute solution of phloroglucinol and aniline nitrate, a cinnabar-red precipitate of benzeneazophloroglucinol is formed after a short time (Weselsky, Ber. 1875, 8, 967; Weselsky and Benedikt, *ibid.* 1879, 12, 226), a distinct precipitate being obtained at the end of 3 hours with only 0·0005 grm. of the substance. A similar reaction is, however, produced by maclurin, decoction of fustic, catechin, and extract of hops (Weselsky, *ibid.* 1876, 9, 217).

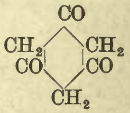
Phloroglucinol in the presence of hydrochloric acid gives a red-violet colour with woody substances; thus a solution containing 0·01 p.c. of phloroglucinol colours pine-shavings, moistened with hydrochloric acid, a distinct red, and a solution containing no more than 0·001 p.c. will give this reaction if the shavings are allowed to remain in the solution for 24 hours (Wiesner, Dingl. poly. J. 1878, 227, 397; Kielmeyer, *ibid.* 584: Wagner, *ibid.* 1878, 228, 173). Phloroglucinol solution (1–30000) gives a definite colour with woodpulp paper (Cross, Bevan and Briggs, Ber. 1907, 40, 3119). Unlike pyrogallol, phloroglucinol is not poisonous.

The desmotropism of phloroglucinol. It has been already stated that the increase in the number of hydroxyl groups in the meta-positions in the benzene nucleus increases the tendency for the compound to react in its desmotropic forms. It is therefore to be expected that in phloroglucinol this tendency would be at its maximum. The experimental facts which show that this phenol reacts in the two desmotropic forms



(Phenol form.)

and



(Keto-form.)

may be summarised as follows:—

The *phenol form* leads to the formation of a tricarbanilido derivative,

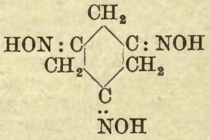
$$C_6H_3(O{\cdot}CO{\cdot}NHC_6H_5),$$

when phloroglucinol is treated with phenyl*iso*cyanate (Goldschmidt and Meissler, Ber. 1890, 23, 269) and causes the phenol to yield well-defined *o*-alkyl derivatives of the type

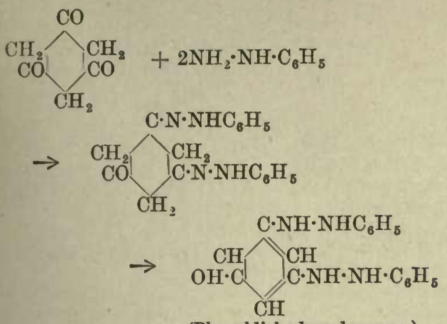
$$C_6H_3(OR)_3$$

when it is alkylated under suitable conditions (Benedikt, Annalen, 1875, 178, 97; Will and Albrecht, Ber. 1884, 17, 2107; Herzig and Zeisel, Monatsh. 1888, 9, 218; Hesse, Annalen, 1893, 276, 328).

The *keto-form* leads to the production of a *trioxime*

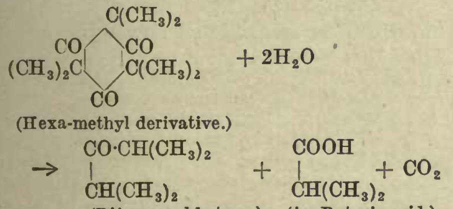


when phloroglucinol is treated with hydroxylamine (Baeyer, Ber. 1886, 19, 159). It is a sandy, crystalline powder which decomposes with explosive violence at 155°. The action of phenylhydrazine leads, in the first instance, to the formation of a salt which on long standing in alcohol passes into phenoldishydrazobenzene

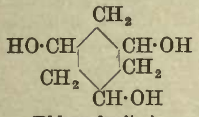

(Phenoldishydrazobenzene.)

(Baeyer and Kochendoerfer, Ber. 1889, 2189). The keto-form is also shown by the readiness with which phloroglucinol reacts with concentrated aqueous ammonia in the cold, yielding, firstly, amino-resorcinol (phloramine, 3 : 5-dihydroxy-1-aminobenzene), and by further action, diaminophenol (5-hydroxy-1:3-diaminobenzene), Pollak (Monatsh. 1893, 14, 401).

Tetra-, penta-, and hexa- alkylated products are formed from phloroglucinol when it is alkylated by alkyl iodides in the presence of alcoholic potash. The alkyl groups in these compounds are not removed by hydriodic acid and are therefore attached to carbon. Their constitution may be illustrated by the hexamethyl derivative which, on heating with concentrated hydrochloric acid at 190°, is transformed into carbon dioxide, di*iso*propyl ketone, and *iso*butyric acid,

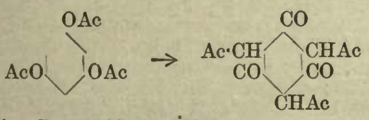

(Hexa-methyl derivative.)
(Di*iso*propyl ketone.) (*iso*-Butyric acid.)

(Herzig and Zeisel, Monatsh. 1888, 9, 217, 882; 1889, 10, 735; 1893, 14, 376). Phloroglucinol is reduced by sodium amalgam in the cold, yielding phloroglucite (*cyclo*-hexanetriol)


(Phloroglucite.)

(W. Wislicenus, Ber. 1894, 27, 357).

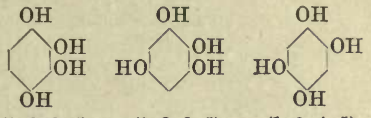
The tendency for derivatives of the phenol form to pass into derivatives of the keto- form is illustrated by the behaviour of phloroglucinol-triacetate which, on heating with an equal part of zinc chloride for 3 hours at 130°, passes into triacetotriketohexamethylene, thus—



(Heller Ber. 1909, 42, 2736).

The dynamic isomerism of phloroglucinol is described by Hedley (Chem. Soc. Trans. 1906, 89, 730).

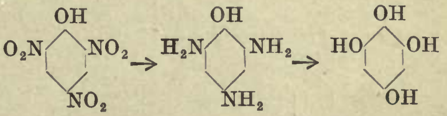
The tetrahydric phenols. There are three theoretically possible tetrahydroxy derivatives of benzene,


(1:2:3:4) (1:2:3:5) (1:2:4:5)

all of which have been prepared; two of them occur naturally in the form of their ethers.

1:2:3:4-*Tetrahydroxybenzene* (Apionol), is the parent substance of the *apiols* (*v.* OILS, ESSENTIAL). It has been prepared synthetically by Einhorn, Coblinger and Pfeiffer (Ber. 1904, 37, 119) by the action of water on the hydrochloride of aminopyrogallol. It forms colourless needles from benzene which melt at 161°. The *tetra-acetyl- derivative* forms needles melting at 136°. The phenol is readily soluble in water, alcohol or ether, and dissolves in alkali forming a pale yellow solution which does not absorb oxygen from the air. The aqueous solution gives an intense blue colour with ferric chloride. A *dimethylmethylene* ether, $C_6H_3(OCH_3)_2{<}^{O}_{O}{>}CH_2$ (Apione), melting at 79°, is formed by the oxidation of Petersilien Apiol. *Tetramethylapionol* $C_6H_2(OCH_3)_4$, melting at 89°, has been prepared by Ciamician and Silber (Ber. 1896, 29, 1808); it is probably identical with the ether prepared from the free phenol and dimethyl sulphate, which melts at 83° (*cf.* Einhorn, Coblinger and Pfeiffer, *l.c.* 105).

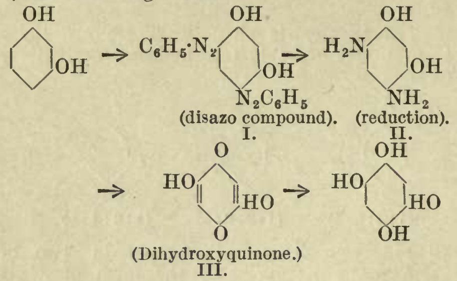
1:2:3:5-*Tetrahydroxybenzene* (oxyphloroglucinol), is formed from picric acid by reduction and elimination of the amino groups by boiling the hydrochloride of the amino compound with water



In the first instance, the trihydroxyaminobenzene $C_6H_2(OH)_3—NH_2$, is formed, but on heating with water at 150° the remaining amino group is eliminated (Will, Ber. 1888, 21, 609, 2020).

The tetrahydric phenol forms slender needles melting at 165°, and the aqueous solution gives a deep-red colour with ferric chloride. The *monomethylether* (2-methoxy-1:3:5-trihydroxybenzene, *iretol*), is formed by the decomposition of the glucoside *iridine* (from violet roots); it forms white needles which melt at 186° and are readily soluble in water. The *trimethyl ether* (1:2:3-trimethoxy-5-hydroxybenzene) has been prepared by Graebe and Suter (Annalen, 1905, 340, 222). It melts at 146° and is identical with Kiliani's antiarol. For other derivatives of this phenol, *see* Bargellini and Bini (Chem. Zentr. 1911, i. 392).

1:2:4:5-*Tetrahydroxybenzene*, is formed from resorcinol in a manner which is indicated by the following scheme:—



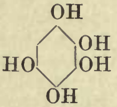
(disazo compound). I.

(reduction). II.

(Dihydroxyquinone.) III.

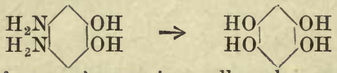
sym-Resorcinoldisazobenzene (I.) is formed by the action of benzene diazonium chloride on resorcinol in the presence of excess of caustic alkali. This is reduced to diaminoresorcinol (II.), which yields diiminoresorcinol on oxidation, a substance which is converted into dihydroxyquinone (III.) on treatment with caustic alkali; the last-named compound is reduced to the tetrahydric phenol by stannous chloride. The tetrahydroxybenzene forms glistening leaflets which melt between 215° and 220°; the aqueous solution becomes rapidly brown on exposure to the air and is at once oxidised to dihydroxyquinone by ferric chloride.

Pentahydric phenol. There is only one theoretically possible pentahydroxy derivative of benzene, namely—



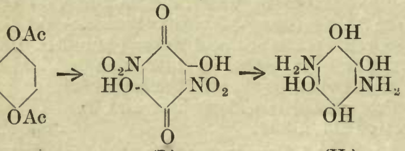
(1:2:3:4:5)

1:2:3:4:5-*Pentahydroxybenzene.* A substance having this constitution has been described by Wenzel and Weidel (Chem. Zentr. 1903 [ii.] 829) as forming colourless crystals insoluble in all the usual organic solvents. Different properties are given to this compound by Einhorn, Coblinger and Pfeiffer (Ber. 1904, 37, 122), who prepared it by the action of water on the hydrochloride of 4:6-diaminopyrogallol

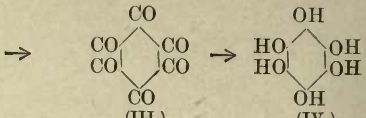


It forms microscopic needles when crystallised from benzene which are readily soluble in ether, alcohol, or ethyl acetate, and which blacken when heated. The aqueous solution gives a dark-red brown colour with ferric chloride. The *penta-acetyl derivative* forms colourless needles which melt with decomposition at 165°.

The only *hexahydric phenol*, hexahydroxybenzene $C_6(OH)_6$, has been prepared by Nietzki and Benckiser (Ber. 1885, 18, 499. 1833) from the diacetyl derivative of hydroquinone in the following way—



(I.) (II.)



(III.) (IV.)

The diacetyl derivative is converted into the so-called 'nitranilic acid' (I.) by the action of nitric and sulphuric acids; this is then reduced to diaminotetrahydroxybenzene (II.) which is oxidised by means of nitric acid to triquinoyl (III.); the latter is then reduced by stannous chloride to hexahydroxybenzene (IV.). The hexahydric phenol forms long needles which cannot be obtained completely colourless; when heated it becomes dark-grey at about 200° without melting. It is sparingly soluble in cold water, but readily dissolves on warming, and is sparingly soluble in alcohol, ether, or benzene. The aqueous solution becomes quickly red-violet on exposure to the air and at once reduces silver nitrate. It is oxidised by concentrated nitric acid to triquinoyl and when its alkaline solution is treated with air, it is converted into tetrahydroxyquinone. The action of dilute alkali yields potassium croconate, and acetic anhydride produces the *hexa-acetyl* derivative which melts at 203° (Maquenne, Bull. Soc. chim. 1887, 48, 64). The potassium salt of hexahydroxybenzene is identical with 'kohlenoxydkalium,' which is prepared by the action of dry carbon monoxide on melted potassium (Gmelin, Pogg. Ann. 1825, 4, 35). J. F. T.

PHENOL COLOURING MATTERS *v.* Oxazine colouring matters.

PHENOL CORALLIN *v.* Aurin.

PHENOLPHTHALEÏN *v.* Triphenylmethane colouring matters.

PHENOPHENANTHRAZINE *v.* Azines.

PHENOSAFRANINE *v.* Azines.

PHENOSAL *v.* Synthetic drugs.

PHENYFORM *v.* Synthetic drugs.

PHENYL. Under this heading will be described the monosubstituted derivatives of benzene, having the general formula C_6H_5R. The radicle C_6H_5 is known as phenyl and is monovalent.

Aminobenzene *v.* Aniline.

Bromobenzene, *Phenyl bromide* C_6H_5Br. Prepared by the interaction of benzene and bromine in the presence of sunlight (Schramm. Ber. 1885, 18, 606), iodine (Rilliet and Ador, *ibid.* 1875, 8, 1287), aluminium chloride (Leroy, Bull. Soc. chim. 1887, 48, 211; Greene, Compt. rend. 90, 40), or aluminium amalgam (Cohen and Dakin, Chem. Soc. Trans. 1899, 894); by the action of phenylhydrazine on perbromacetone (Levy and Jedlicka, Annalen, 249, 84); by the action of sulphur bromide and nitric acid on benzene (Edinger and Goldberg, Ber. 1900, 33, 2884); by diazotising aniline in the presence of copper, sulphuric acid, and potassium bromide (Sandmeyer, *ibid.* 1884, 17, 2650); for electrolytic method *v.* Votoček and Zenišek (Chem. Zentr. 1899, i. 1146).

Bromobenzene is a colourless liquid, b.p. 156·6° (758·6 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 70); m.p. —30·5° (corr.) (Schneider, *ibid.* 22, 232; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1·5105, 15°/15° 1·4991, 25°/25° 1·4886, 50°/50° 1·4681, 100°/100° 1·4416; magnetic rotation (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Ramsay and Young, *ibid.* 1885, 646, 655; Young, *ibid.* 1889, 488, 506; Kahlbaum, Zeitsch. physikal. Chem. 26, 584); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 386). Heated with aluminium chloride, bromobenzene yields benzene and isomeric dibromobenzenes (Dumreicher, Ber. 1882, 15, 1867); with sodium methoxide at 200° anisole, phenol, and a small quantity of benzene are formed (Blau, Monatsh. 7, 626). Sodium in ether yields hydrocarbons of high molecular weight and a dark-blue substance (Weiler, Ber. 1896, 29, 115; Mohr, J. pr. Chem. 1909, [ii.] 80, 315); ethyl oxalate and sodium in absolute ether yield benzoic acid and triphenylcarbinol (Frey, Ber. 1895, 28, 2315). Heated with sulphuric acid, bromobenzene yields 1 : 3 : 5-dibromobenzene sulphonic acid and a bromobenzene disulphonic acid (Herzig, Monatsh 2, 192); nitric acid (sp.gr. 1·5) gives 1 : 2 : 4-bromodinitrobenzene together with *o*- and *p*-bromonitrobenzenes (Bandrowski, Bull. Acad. Sci. Cracow, 1900, 193). Hydriodic acid and phosphorus are without action on bromobenzene at 218° (Klages and Liecke, J. pr. Chem. [ii.] 61, 319).

Chlorobenzene, *Phenyl chloride,* C_6H_5Cl. Prepared by the action of phosphorus pentachloride on phenol (Gerhardt and Laurent, Annalen, 75, 79); by heating benzene with thionyl chloride at 150° (Dubois, Zeitsch. Chem. 1866, 705) or with sulphur chloride at 250° (Schmidt, Ber. 1878, 11, 1173); by the electrolysis of a strong hydrochloric acid solution of cupric chloride in the presence of benzene diazonium chloride using copper electrodes (Votoček and Zenišek, Chem. Zentr. 1899, i. 1146; *cf.* Walter, J. pr. Chem. 1896, [ii.] 53, 427); by diazotising aniline and heating the product with cuprous chloride (Sandmeyer, Ber. 1884, 17, 1633); by the action of chlorine on benzene in the presence of aluminium chloride (Mouneyrat and Pouret, Compt. rend. 1898, 127, 1026), ferric chloride (Thomas, *ibid.* 1898, 126, 1212), or a mixture of finely divided iron and ferric chloride (D. R. P. 219242; J. Soc. Chem. Ind. 1910, 619).

Chlorobenzene is a colourless liquid, b.p. 131·8° (757 mm.) (Perkin, Chem. Soc. Trans. 1896, 387; *cf.* Ramsay and Young, *ibid.* 1885, 642, 654; Fuchs, Zeitsch. angew. Chem. 1898, 869); m.p. −45° (corr.) (Schneider, Zeitsch. physikal. Chem. 19, 155); sp.gr. 4°/4° 1·1230, 15°/15° 1·1125, 25°/25° 1·1042, 50°/50° 1·0868, 100°/100° 1·0623 (Perkin, *l.c.*); critical temperature 359·2° (Young, Zeitsch. physikal. Chem. 11, 590; Schneider, *ibid.* 70, 626); vapour pressure (Young, Chem. Soc. Trans. 1889, 90, *et seq.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 811); magnetic rotation (Perkin, *l.c.*); dielectric constant (Jahn and Möller, Zeitsch. physikal. Chem. 13, 387). By passing the vapour of chlorobenzene over red-hot iron filings, diphenyl, mono- and di- chlorodiphenyl and diphenylbenzene are formed (Kramers, Annalen, 189, 135). On heating with sodium in carbon tetrachloride, triphenylmethane, hexaphenylbenzene and diphenyl are produced (Schmidlin, Compt. rend. 1903, 137, 59), whilst with aluminium chloride the products are the chlorides of 4 : 4′- and 2 : 4′-dichlorobenzophenones (Norris and Green, Amer. Chem. J. 1901, 26, 492; Norris and Tweig, *ibid.* 1903, 30, 392). Chlorine in the sunlight yields $C_6H_5Cl.Cl_4$, $C_6H_4Cl_8$, and other products; in the presence of dilute sodium hydroxide, α- and β-chlorobenzene hexachlorides are produced (Matthews, Chem. Soc. Trans. 1891, 167; 1892, 103). Bromine in the presence of aluminium chloride yields *p*-chlorobromobenzene and other products (Mouneyrat and Pouret, Compt. rend. 1899, 129, 605); sulphuric acid and iodine yield chlorodiiodobenzene ($Cl : I_2 = 1 : 2 : 4$), chlorotriiodobenzene ($Cl : I_3 = 1 : 2 : 4 : 6$) and other products (Istrati, Chem. Zentr. 1897, i. 1161). Chlorobenzene remains unchanged on heating with hydriodic acid and phosphorus at 302° (Klages and Liecki, J. pr. Chem. [ii.] 61, 319). Nitric acid at 0° gives *o*-, *m*-, and *p*-chloronitrobenzenes, the yields being 29·8, 0·3 and 69·9 p.c. respectively (Holleman, Proc. K. Akad. Wetensch. Amsterdam, 1905, 7, 266). Oxidised by sulphuric acid and manganese dioxide to formic and *p*-chlorobenzoic acids. Has been recommended as a solvent for resins (Andès, Chem. Rev. Fett. Harz-Ind. 1906, 13, 32). For stability of halogenated benzenes *v.* Löwenherz (Zeitsch. physikal. Chem. 1899, 29, 401); Vandevelde (Chem. Zentr. 1898, i. 438).

Iodobenzene, *Phenyl iodide,* C_6H_5I. Prepared by the action of phosphorus triiodide on phenol (Scrugham, Annalen, 92, 318); by heating a mixture of benzene and iodine with aluminium chloride (Green, Compt. rend. 90, 40), ferric chloride (Meyer, Annalen, 231, 195), or with sulphuric acid (Neumann, *ibid.* 241, 84; Istrati and Georgescu, Chem. Zentr. 1892, i. 625), in the last method higher halogenated compounds also being formed; by the interaction of benzene and sulphur iodide in the presence of nitric acid (Edinger and Goldberg, Ber. 1900, 33, 2876); by heating phenyl hydrazine with excess of iodine in potassium iodide solution (Meyer, J. pr. Chem. [ii.] 36, 115); by heating benzene with potassium iodate and dilute sulphuric acid (Peltzer, Annalen, 136, 197); by heating sodium benzoate with iodine monochloride (Schützenberger, J. 1861, 349; 1862, 251).

Iodobenzene is a colourless liquid, b.p. 188·36° (755·75 mm.) (Feitler, Zeitsch. physikal. Chem. 4, 71); m.p. −28·5° (corr.) (Schneider, *ibid.* 19, 157; *cf.* Haase, Ber. 1893, 26, 1053); sp.gr. 4°/4° 1·8551, 15°/15° 1·8401, 25°/25° 1·8283, 50°/50° 1·8067, 100°/100° 1·7832 (Perkin, Chem. Soc. Trans. 1896, 1243); vapour pressure (Young, *ibid.* 1889, 490, 510); heat of combustion 770·0 Cal. (Berthelot, Compt. rend. 130, 1098); magnetic rotation (Perkin, *l.c.*); absorption spectrum (Pauer, Chem. Zentr. 1896, i. 1122; Purvis, Chem. Soc. Trans. 1911, 2318). Iodobenzene is reduced to benzene by sodium amalgam in alcohol; with aluminium chloride it yields benzene, isomeric diiodobenzenes, hydrochloric acid and iodine (Dumreicher, Ber. 1882, 15, 1868); with silver nitrate at 145° picric acid is formed (Geuther, Annalen, 245, 100); oxidised by Caro's acid to iodoxybenzene (Bamberger and Will, Ber. 1900, 33, 534).

Nitric acid (sp.gr. 1·5) yields *o*- and *p*-nitroiodobenzenes (Korner, Gazz. chim. ital. 4, 305); chlorine in chloroform solution gives a dichloride (Willgerot, J. pr. Chem. [ii.] 33, 155). Iodobenzene is unchanged by heating with hydriodic acid and phosphorus at 182° (Klages and Liecke, *ibid.* 61, 319); action of ferric chloride and ferric bromide *v.* Thomas (Compt. rend. 128, 1577).

Nitrobenzene *v.* BENZENE.

Phenyl azoimide, Triazobenzene, Diazobenzeneimide $C_6H_5N_3$. Prepared by the action of ammonia (Greiss, Annalen, 137, 68) or of phenylhydrazine (Oddo, Gazz. chim. ital. 20, 798) on diazobenzene perbromide; by the action of nitrous acid on phenylhydrazine at 0° (Dimroth, Ber. 1902, 35, 1032); by passing nitrosyl chloride into a solution of phenylhydrazine in glacial acetic acid (Tilden and Millar, Chem. Soc. Trans. 1893, 257); by heating nitrosophenylhydrazine with dilute potassium hydroxide (E. Fischer, Annalen, 190, 92) or with alcoholic hydrochloric acid (O. Fischer, Ber. 1886, 19, 2995); by the interaction of stannous chloride and diazobenzene chloride in hydrochloric acid solution (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 99), or of diazobenzene sulphate and sodium azide or hydrazine (Noelting and Michel, Ber. 1893, 26, 86, 89); by the action of sodium hypochlorite on phenylsemicarbazide or on phenylazocarbonamide (Darapsky, *ibid.* 1907, 40, 3033); or together with other products, by the interaction of phenylhydroxylamine and hydroxylamine in the presence of a mineral acid (Bamberger, *ibid.* 1902, 35, 3895).

Phenyl azoimide is a pale yellow oil having an aromatic-ammoniacal smell, b.p. 73·5° at 22–24 mm.; sp.gr. 0°/4° 1·12399 (Oddo), 10°/10° 1·0980, 25°/25° 1·0853 (Perkin, Chem. Soc. Trans. 1896, 1245); insoluble in water, soluble in alcohol or ether. Explodes on distillation at atmospheric pressure. On heating with concentrated hydrochloric acid, it decomposes into nitrogen and *o*- and *p*-chloranilines (Greiss, Ber. 1886, 19, 313). Strong sulphuric acid causes explosions, but very dilute acid yields *p*-aminophenol. Excess of bromine gives tribromaniline (Culmann and Gasiorowski, J. pr. Chem. [ii.] 40, 97). Reduction in alcoholic solution with sodium analgam gives hydrazobenzene (Curtius, *ibid.* [ii.] 52, 210), with zinc and hydrochloric acid ammonia and aniline. Hydrazine hydrate yields benzene, ammonia and nitrogen (Curtius and Dedichen, *ibid.* [ii.] 50, 252). Phenyl azoimide yields triazo compounds by condensation with substances containing a reactive methylene group (Dimroth, Ber. 1902, 35, 4041); it reacts with alkyl magnesium halides forming diazoamino compounds (Dimroth, *ibid.* 1903, 36, 909).

Phenylcarbimide, Phenyl ***iso*****cyanate, Carbanil** $C_6H_5N:C:O$. Prepared by distilling oxanilide (Hofmann, Annalen, 74, 33), diphenylurea (J. 1858, 348) or phenylurethane (Ber. 1870, 3, 655) with phosphorus pentoxide; by distilling oxanilyl chloride (Aschan, *ibid.* 1890, 23, 1825); by heating phenylthiocarbimide with mercuric oxide (Kühn and Liebert, *ibid.* 1536); by decomposing diazobenzene sulphate with potassium cyanate and copper powder (Gattermann, *ibid.* 1225; 1892, 25, 1086); by passing phosgene over fused diphenylurea or better over fused aniline hydrochloride (Hentzchel, *ibid.* 1884, 17, 1284; *cf.* D. R. P. 19919; Frdl. i. 578).

Phenylcarbimide is a colourless liquid, the vapour of which excites tears; b.p. 166° at 769 mm. (Hofmann, Ber. 1885, 18, 764); sp.gr. 1·092 at 15°. With water it yields diphenylurea, with alcohol phenylurethane, and with ammonia monophenylurea. It is much used as a reagent for detecting the presence of hydroxyl and imino groups: condensation with alcohols (*v.* Hofmann, Annalen, 74, 16; Ber. 1871, 4, 249; Tessmer, *ibid.* 1885, 18, 968; 1886, 19, 2606; Snape, Chem. Soc. Trans. 1885, 770; Gumpert, J. pr. Chem. [ii.] 32, 278; Bloch, Bull. Soc. chim. [iii.] 31, 49, 71): with phenol (*v.* Leuckhart and Schmidt, Ber. 1885, 18, 2338). By heating with dilute hydrochloric acid, ammonium chloride, aniline, and carbon dioxide are produced; with acetic acid, diphenylurea, and traces of aniline and acetanilide (Dieckmann and Kammerer, *ibid.* 1907, 40, 373); with acetic anhydride at 170° acetanilide, benzene and carbon dioxide (Gumpert, J. pr. Chem. [ii.] 31, 121); with potassium acetate at 100° triphenyl*iso*cyanurate (Hofmann, Ber. 1885, 18, 765). It combines with prussic acid in benzene after the addition of a few drops of pyridine to form cyanoformanilide (Dieckmann and Kammerer, *ibid.* 1905, 38, 2977), and with hydrogen chloride to give chloroformanilide (Hentzchel, *ibid.* 1885, 18, 1178). Heated in sealed tubes at 180° it yields carbodiphenylimide (Stollé, *ibid.* 1908, 41, 1125); heated with zinc it gives aniline. It combines with two atoms of chlorine or bromine. With benzene in the presence of aluminium chloride it gives benzanilide (Leuckhart, *ibid.* 1885, 18, 873; J. pr. Chem. [ii.] 41, 301).

Phenyl cyanide, benzonitrile *v.* NITRILES.

Phenyl ***iso*****cyanide, Phenylcarbylamine** *v.* NITRILES.

Phenylhydroxylamine *v.* HYDROXYLAMINE.

Phenylthiocarbimide, Phenyl ***iso*****thiocyanate, Phenyl mustard oil** $C_6H_5N:C:S$. Prepared by heating diphenylthiourea with phosphorus pentoxide (Hofmann, J. 1858, 349), concentrated hydrochloric acid (Weith and Merz, Zeitsch. Chem. 1869, 589), phosphoric acid (Hofmann, Ber. 1882, 15, 986), acetic anhydride (Werner, Chem. Soc. Trans. 1893, 400), or with phthalic anhydride (Dunlap, Amer. Chem. J. 1896, 18, 332), in the last method phthalanilic acid also being formed. By heating phenyl *iso*cyanide with sulphur (Weith, Ber. 1873, 6, 211), phenyl thiohydantoin with carbon disulphide (Dixon, Chem. Soc. Trans. 1897, 628) or phenyl carbimide or phenylurethane with phosphorus pentasulphide at 160° (Michael and Palmer, Amer. Chem. J. 6, 258); by the interaction of thiophosgene and aniline (Rathke, Ber. 1870, 3, 861); together with the hydriodide of triphenylguanidine and aniline by heating an alcoholic solution of diphenylthiourea with iodine (Hofmann, *ibid.* 1869, 2, 453; Rudnew, J. Russ. Phys. Chem. Soc. 10, 184).

Phenylthiocarbimide is an unpleasant smelling liquid, b.p. 221° (corr.); sp.gr. 4°/4° 1·1477, 15°/15° 1·1382, 25°/25° 1·1314 (Perkin, Chem. Soc. Trans. 1896, 1204). By boiling with water diphenylthiourea, sulphuretted hydrogen and carbon dioxide are produced (Bamberger, Ber. 1881, 14, 2462); glacial acetic acid at 130° yields acetanilide, carbon oxysulphide, and diphenylurea (Werner, Chem. Soc. Trans. 1891, 548; Claus and Völtzkow, Ber. 1881, 14, 445; Gumpert, J. pr. Chem. [ii.] 32, 294; Cain and Cohen, Chem. Soc. Trans. 1891, 327); whilst with thioacetic acid it gives acetanilide. It combines with ammonia and substituted amines yielding substituted thioureas. Chlorine forms an addition product; copper powder at 200° yields benzonitrile. Reduction with hydrochloric acid in absolute alcohol gives aniline and thioformaldehyde (Pinner, Ber. 1881, 14, 1083), whilst aluminium amalgam in neutral solution gives diphenylthiourea and methyl mercaptan (Gutbier, *ibid.* 1901, 34, 2033). Sulphuric acid gives carbon disulphide and diphenylthiourea (Proskauer and Sell, *ibid.* 1876, 9, 1266); malonic acid yields diphenylurea and acetanilide, succinic acid succinanil, and sebacic acid, the dianilide of the acid (Bénech, Compt. rend. 130, 292). By condensing phenylthiocarbimide with aliphatic monohydroxyalcohols, phenylthiourethanes are produced (Hofmann, Ber. 1870, 3, 772; Orndorff and Wheeler, Amer. Chem. J. 1899, 22, 458), with phenol phenyl-ψ-phenylthiocarbamic acid (Dixon, Chem. Soc. Trans. 1890, 268; Snape, *ibid.* 1896, 98) and with aromatic hydrocarbons or phenol ethers substituted thioureas (Gattermann, J. pr. Chem. 1899, [ii.] 59, 572). Bromine and alcohol in ethereal solution give a dibromo additive compound and phenylthiocarbimide oxide (Fromm and Heyden, Ber. 1909, 42, 3800; Freund and Bachrach, Annalen, 285, 184; Hantzsch and Wolverkampf, *ibid.* 331, 265).

Phenylthiocyanate, $C_6H_5S{\cdot}C\vdots N$. Prepared by the action of thiocyanic acid (Billeter, Ber. 1874, 7, 1753) or of cuprous thiocyanate (Gattermann and Haussknecht, *ibid.* 1890, 23, 739) on diazobenzene sulphate; by passing cyanogen chloride into an alcoholic solution of the lead salt of thiophenol (Billeter, *l.c.*).

It is a colourless liquid having a leek-like smell, b.p. 231° (corr.); sp.gr. 1·155 at 17·5°. Concentrated hydrochloric acid at 180°–200° yields thiophenol, ammonia, and carbon dioxide; alcoholic potassium hydrosulphide gives thiophenol.

PHENYLACETIC ACID, *a-toluic acid*

$$C_6H_5{\cdot}CH_2{\cdot}CO_2H$$

is prepared by the hydrolysis of benzyl cyanide (Cannizzaro, Annalen, 1855, 96, 247; Mann, Ber. 1881, 14, 1645; Staedel, *ibid.* 1886, 19, 1949). It has been obtained by fusing phenylmalonic acid (Wislicenus, *ibid.* 1894, 27, 1094); by boiling vulpic acid with baryta (Möller and Strecker, Annalen, 1860, 113, 64); by fusing atropic acid with potassium hydroxide (Kraut, *ibid.* 1868, 148, 242); by reducing mandelic acid (Brown, Zeitsch. Chem. 1865, 443); by heating phenylchlorovinyl ethyl ether with alcoholic potassium hydroxide (Nef, Annalen, 1899, 308, 318); and by decomposing by water the product of the action of carbon dioxide on an ethereal solution of magnesium benzyl chloride (Zelinsky, Ber. 1902, 35, 2692). It occurs together with phenylpropionic acid among the putrefactive decomposition products of certain proteins (Salkowski, Ber. 1879, 12, 649; Zeitsch. physiol. Chem. 1888, 2, 420; 1892, 9, 507), and the two are readily separated by the fractional crystallisation of the zinc salts (Salkowski, *ibid.* 1892, 10, 150). According to Engler and Löw (Ber. 1893, 26, 1436) the presence of benzenoid hydrocarbons in mineral oil may not be exclusively due to a pyrogenetic process, but may arise from the phenylacetic acid produced by the decay of proteid matter.

Phenylacetic acid crystallises in thin leaves, m.p. 76·5°, b.p. 265·5° (corr.), 144·2°–144·8°/12 mm. (Anschutz and Berns, Ber. 1887, 20, 1390), sp.gr. 1·0778 at 83°, 1·0334 at 135°/4° (Möller and Strecker, *l.c.*), or 1·228 at 4° (Schröder, Ber. 1879, 12, 1612); the magnetic rotatory power is 12·743 (Perkin, Chem. Soc. Trans. 1896, 1079); and the molecular heat of combustion 933·2 Cal. (Stohmann, Kleber and Langbein, J. pr. Chem. 1889, [ii.] 40, 128). In its physiological action phenylacetic acid differs markedly from phenylpropionic acid which is completely oxidised to benzoic acid when administered as a food to a dog, whilst phenylacetic acid is converted under similar conditions into *phenaceturic acid* $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m.p. 143° (E. and H. Salkowski, Ber. 1879, 12, 653). When fed to fowls phenylacetic acid combines with ornithine to produce *phenylaceto-ornithuric acid*

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}NH[CH_2]_3CH(NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5)CO_2H$$

(Totani, Zeitsch. physiol. Chem. 1910, 68, 75).

Salts.—Calcium salt $(C_8H_7O_2)_2Ca,3H_2O$ (Kraut, *l.c.*); barium salt $(C_8H_7O_2)_2Ba,3H_2O$ loses $2\frac{1}{2}H_2O$ at 150°; lead salt

$$(C_8H_7O_2)_2Pb,H_2O$$

(Guye, J. 1884, 468); silver salt $C_8H_7O_2Ag$; yttrium salt $(C_8H_7O_2)_3Y,3H_2O$ is insoluble (Pratt and James, J. Amer. Chem. Soc. 1911, 33, 1330); the brucine salt

$$C_{23}H_{26}O_4N_2{\cdot}C_8H_8O_2,1\tfrac{1}{2}H_2O$$

has m.p. 130°–131°, $[\alpha]_D^{20°}-30{\cdot}5°$ in 5 p.c., and $-32{\cdot}2°$ in $2\frac{1}{2}$ p.c. chloroform solution (Hilditch, Chem. Soc. Trans. 1908, 1388).

Esters.—Methyl ester, b.p. 220°, sp.gr. 1·044 at 16° (Radzisjewski, Ber. 1869, 2, 208); chloromethyl ester, b.p. 138°–140°/15 mm. (Descudé, Compt. rend. 1902, 134, 716); ethyl ester, b.p. 227·3°, sp.gr. 1·0555 at 4°/4°; 1·0462 at 15°/15°, or 1·039 at 25°/25° (Perkin, Chem. Soc. Trans. 1896, 69, 1238); propyl ester, b.p. 238°, sp.gr. 1·0142 at 18° (Hodgkinson, *ibid.* 1880, 34, 483); *iso*butyl ester, b.p. 247° (Hodgkinson, *l.c.*); active amyl ester, b.p. 265°–266°/722·7 mm., sp.gr. 0·982 at 20°/4°; n_D 1·4872 at 21°; $[\alpha]_D+3{\cdot}84°$ at 22° (Guye and Chavanne, Bull. Soc. chim. 1896, [iii.] 15, 292); benzyl ester, b.p. 317°–319°, sp.gr. 1·101 (Slawik, Ber. 1874, 7, 1056), b.p. 270°/160 mm., sp.gr. 1·0938 at 170° (Hodgkinson, *l.c.*); menthyl ester, b.p. 192°–197°/10 mm.; sp.gr. 1·002 at 20°/4°; 0·9400 at 100°/4°; $[\alpha]_D-68{\cdot}70°$ at 20° (Tschugaeff, Ber. 1898, 31, 2451; Cohen and Dudley, Chem. Soc. Trans. 1908, 1749); phenyl ester, m.p. 42°, b.p. 158°/17 mm. (Stoermer and Biesenbach, Ber. 1905, 38, 1958); phenylethyl ester, m.p. 28°, b.p. 330° (von Soden and Rojahn, *ibid*, 1900, 33, 1720).

Phenylacetyl chloride $C_6H_5{\cdot}CH_2{\cdot}COCl$ has b.p. 95·1°–95·8°/12 mm., 102·5°/17 mm., 104°–105°/23 mm., or 170°/250 mm.; sp.gr. 1·16817 at 20°/4°, 1·856 at 4°/4°, 1·1753 at 11°/15°, 1·1674 at 15°/15°; and yields the *anhydride*, m.p. 72·5°, on heating with oxalic acid (Anschütz and Berns, Ber. 1887, 20, 1389; Schott, *ibid.* 1896, 29, 1986; Perkin, Chem. Soc. Trans. 1896, 69, 1244).

Phenylacetamide $C_6H_5·CH_2·CO·NH_2$ has m.p. 154°–155°, b.p. 281°–284° (Weddige, J. pr. Chem. 1873, [ii.] 7, 100); the *diethylamide* has m.p. 86°, b.p. 295°–297° (corr.); the *diphenylamide* has m.p. 72° (Hausknecht, Ber. 1889, 22, 324); the *hydrazide* has m.p. 116°; the *azoimide* is a colourless oil and yields with bromine a crystalline compound, m.p. 121° (Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314). *Phenylaceturonitrile* $C_6H_5·CH_2·CO·NH·CH_2·CN$ has m.p. 90·5°; *ethyl phenylaceturate,* m.p. 82° (Klages and Haack, Ber. 1903, 36, 1646); *phenylacetylurethane,* m.p. 113° (Diels, *ibid.* 1903, 36, 736).

Phenylacetic acid and the derivatives described above contain a methylene group of similar reactivity to that in malonic acid, ethyl acetoacetate, &c., and they therefore undergo the Claisen condensation (Boëseken, Rec. trav. chim. 1896, 15, 161; Hodgkinson, Chem. Soc. Proc. 1886, 188); form condensation products with aldehydes (Röhmer, Ber. 1898, 31, 281; Boetzelen, J. pr. Chem. 1901, [ii.] 64, 314); react with ethyl nitrate and nitrite (Müller, Ber. 1883, 16, 1617; 2985; Wislicenus and Grützner, *ibid.* 1909, 42, 1930; Noelting and Kadiera, *ibid.* 1906, 39, 2056); and form halogen substituted and amino derivatives that contain an asymmetric carbon atom and have been resolved into their optically active constituents (Easterfield, Chem. Soc. Trans. 1891, 71; Walden, Ber. 1895, 28, 1287; Zeitsch. physikal. Chem. 1895, 17, 705; Bischoff, Ber. 1897, 30, 276; Kossel, *ibid.* 1891, 24, 4145; Stadnikoff, J. Russ. Phys. Chem. Soc. 1906, 38, 943; Ehrlich and Wendel, Biochem. Zeitsch. 1908, 8, 438; Fischer and Weichhold, Ber. 1908, 41, 1286; Betti and Mayer, *ibid.* 2071).

In addition to the derivatives already described or to which reference has been made, phenylacetic acid forms a series of substituted derivatives in which the substituent has replaced hydrogen of the benzene ring. With the exception of a *dihydroxy* derivative (*homogentisic acid*), the compounds belonging to this series are not of sufficient importance for the purpose of this article to merit a detailed description; and for the preparation and properties of the halogen, nitro and nitro-halogen, &c., derivatives, *see* Jackson and Lowery, Ber. 1877, 10, 1209; Jackson and Field, Amer. Chem. J. 2, 85; Mabery and Jackson, Ber. 1878, 11, 55; Zincke and Böttcher, Annalen, 1905, 343, 100; Maxwell, Ber. 1879, 12, 1764; Bedson, Chem. Soc. Trans. 1880, 90; Gabriel, Ber. 1881, 14, 2341; 1882, 15, 834, 1992; Gabriel and Meyer, *ibid.* 1881, 14, 823; Gabriel and Borgmann, *ibid.* 1883, 16, 2064; Meyer, Chem. Zentr. 1885, 516; Ber. 1888, 21, 1306; Bedson, *ibid.* 1877, 10, 530, 1657; Jackson and Robinson, Amer. Chem. J. 11, 541; Jackson and Carlton, *ibid.* 1904, 31, 360; Jackson and Shortt Smith, *ibid.* 1904, 32, 168; Reissert, Ber. 1908, 41, 3921; Traube, *ibid.* 1882, 15, 2110; and Mellinghoff, *ibid.* 1889, 22, 3207).

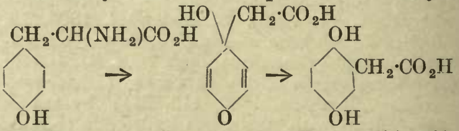
Homogentisic acid, 2 : 5-*dihydroxyphenylacetic acid, quinolacetic acid*

$$C_6H_3(OH)_2CH_2·CO_2H,$$

occurs in the urine of certain individuals suffering from *alcaptonuria*, the name *alcapton* being applied by Bödeker (Zeit. rat. Med. 1859, 7, 130) to a reducing substance occurring in certain urines that became brown on addition of alkali in the presence of oxygen (*compare* also Kirk, Brit. Med. J. 1888, 2, 232; 1889, 2, 1149). The acid was first isolated and identified by Wolkow and Baumann (Zeitsch. physiol. Chem. 1894, 15, 228), and the name *homogentisic acid* applied to it. Homogentisic acid occurs also in the blood serum of alcaptonurics (Abderhalden and Falta, Zeitsch. physiol. Chem. 1903, 39, 143); but the statements that it is found in sugar-beet juice (Gonnermann, Chem. Zeit. 1899, 23, 213) and in seedlings (Bertel, Chem. Zentr. 1903, i. 178) have not been confirmed by later investigations (Schulze, Zeitsch. physiol. Chem. 1907, 50, 508; Schulze and Castoro, *ibid.* 1906, 48, 396).

Origin of homogentisic acid in the organism. According to Embden (Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304); Wolkow and Baumann, (*l.c.*); Mittelbach (Chem. Zentr. 1901, ii. 1213); Neubauer and Falta (Zeitsch. physiol. Chem. 1904, 42, 81); Blum (Arch. exp. Path. Pharm. 1908, 59, 273); and Neubauer (Deut. Archiv. Klin. Med. 1909, 95, 211), homogentisic acid is a degradation product of phenylalanine and tyrosine, and in the normal individual it undergoes ultimate oxidation to carbon dioxide and water, but owing to an idiosyncrasy in metabolism the alcaptonuric excretes the acid without further change. Dakin and Wakeman (J. Biol. Chem. 1911, 9, 139, 151), however, maintain that alcaptonuria represents a condition in which the formation of homogentisic acid is abnormal as well as the failure to effect is katabolism when formed, for such individuals have not lost their power to katabolise simple derivatives of phenylalanine and tyrosine (*e.g. p*-methylphenylalanine or *p*-methoxyphenylalanine) provided their structure is such that the formation of substances of the type of homogentisic acid is excluded.

The mechanism of the change whereby tyrosine is converted into homogentisic acid is somewhat obscure. According to Blum, *l.c.*, Friedmann (Beitr. Chem. Physiol. Path. 1908, 11, 304), Neubauer, *l.c.*, Suwa (Zeitsch. physiol. Chem. 1911, 72, 113), the side chain is first degraded, then a relative change of position of the side chain and the hydroxyl group, and a secondary oxidation take place concurrently

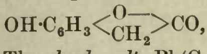


Tyrosine. Homogentisic acid.

The average excretion of homogentisic acid in cases of alcaptonuria is fairly uniform (Garrod and Hele, J. Physiol. 1905, 33, 198); the amount is, however, increased by the administration of tyrosine or phenylalanine, or of peptides or proteids that yield tyrosine on hydrolysis (Embden, Zeitsch. physiol. Chem. 1895, 17, 182; 18, 304; Falta and Langstein, *ibid.* 1903, 37, 513; Neubauer and Falta, *ibid.* 1904, 42, 81; Abderhalden and Bloch, *ibid.* 1907, 52, 435; 53, 464; Abderhalden, Massini, *ibid.* 1910, 66, 140; Blum, *l.c.*; Neubauer, *l.c.*).

Homogentisic acid has been synthesised by heating quinol dimethyl ether dissolved in carbon disulphide with ethylchloracetate and aluminium chloride, and subsequent hydrolysis with red phosphorus and fuming hydriodic acid of the methyl ether of homogentisic acid thus obtained (Osborne, Proc. Physiol. Soc. 1903, 13, 14).

Homogentisic acid forms prisms that melt at 146·5°–147°, and pass into the *lactone*



$$OH{\cdot}C_6H_3{<}\begin{matrix}O{-}\\CH_2\end{matrix}{>}CO,$$

m.p. 191°. The *lead salt* $Pb(C_8H_7O_4)_2,3H_2O$ has m.p. 214°–215°, is soluble in 675 parts of water at 20°, and advantage is taken of this sparing solubility in the isolation of the acid. The *ethyl ester* has m.p. 119°–120°; the *dimethyl ether* $(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CO_2H$ has m.p. 124·5°; and its *methyl ester* $(OMe)_2C_6H_3{\cdot}CH_2{\cdot}CO_2Me$, m.p. 45° (Wolkow and Baumann, Zeitsch. physiol. Chem. 1894, 15, 228; Baumann and Fränkl, *ibid.* 20, 221). *Dibenzoylhomogentisamide* has m.p. 204° (Orton and Garrod, J. Physiol. 1901, 27, 89). Homogentisic acid reduces copper and silver salts readily, gives a blue colour with ferric chloride, and yields gentisic acid (2 : 5-dihydroxybenzoic acid) and quinol on fusion with potassium hydroxide at 196°–198°. For the chemistry of the colour reactions afforded by homogentisic acid with amines, *see* Mörner, Zeitsch. physiol. Chem. 1910, 69, 329.

Estimation.—Homogentisic acid in urine is estimated by measuring its reducing action on silver nitrate. 10 c.c. of the filtered urine, 10 c.c. of ammonia solution (8 p.c.), 20 c.c. of N/10 silver nitrate solution are placed in a flask, after five minutes 5 drops of calcium chloride and 10 drops of ammonium carbonate solution are added, the solution made up to 50 c.c., and the silver estimated in half the filtrate. One molecule of homogentisic acid reduces 4 atoms of silver (Baumann, Zeitsch. physiol. Chem. 1895, 16, 268; Denigés, J. Pharm. Chem. 1897, [vi.] 5, 50; Garrod and Hurtley, J. Physiol. 1905, 33, 206).

PHENYLALANINE, *β-phenyl-α-aminopropionic acid, α-aminohydrocinnamic acid*

$$C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CO_2H$$

was discovered in the etiolated seedlings of *Lupinus luteus* (Schulze and Barbieri, Ber. 1879, 12, 1924; 1881, 14, 1785), and occurs in many other germinating plants (Schulze, Zeitsch. physiol. Chem. 1888, 12, 405; 1892, 17, 193; 1894, 20, 306; 1896, 22, 411; 1900, 30, 241). Winterstein (*ibid.* 1904, 41, 485) found it among other products of proteid hydrolysis in Emmenthaler cheese; and Abderhalden and Barker (*ibid.* 1904, 42, 524) showed that it occurs in the urine of dogs suffering from phosphorus poisoning.

The naturally occurring phenylalanine (*l*-phenylalanine) originates from the protein of the germinating plant, and it can also be readily obtained by the hydrolysis of a large number of proteids (*v.* Proteins) by means of hydrochloric acid, stannous chloride, or baryta (Schulze and Barbieri, Ber. 1883, 16, 1711; Zeitsch. physiol. Chem. 1884, 9, 63); it occurs in that fraction of the esterified products of hydrolysis that boils at 130°–160°/0·5 mm., and is isolated by precipitation from the mixed esters by means of water (Fischer, *ibid.* 1901, 33, 412), or by means of its sparingly soluble copper salt (Schulze and Barbieri, J. pr. Chem. 1883, [ii.] 27, 337; *compare* Schulze and Winterstein, Ber. 1902, 35, 210).

Synthesis.—The constitution of phenylalanine was determined by Erlenmeyer and Lipp (Ber. 1882, 15, 1006), who synthesised it from phenylacetaldehyde, hydrogen cyanide, and ammonia

$$C_6H_5{\cdot}CH_2{\cdot}CHO \rightarrow C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CN$$
$$\rightarrow C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CO_2H.$$

Plöchl (*ibid.* 1883, 16, 2815; 1884, 17, 1616) obtained it by the reduction and subsequent hydrolysis of α-benzoylaminocinnamic acid obtained by the condensation of benzaldehyde with hippuric acid in the presence of acetic anhydride—

$$C_6H_5{\cdot}CHO + CH_2(NH{\cdot}COPh)CO_2H$$
$$\rightarrow C_6H_5{\cdot}CH : C(NH{\cdot}COPh)CO_2H$$
$$\rightarrow C_6H_5{\cdot}CH_2{\cdot}CH(NH{\cdot}COPh)CO_2H$$
$$\rightarrow C_6H_5{\cdot}CH_2{\cdot}CH(NH_2)CO_2H.$$

For a complete explanation of the mechanism of this reaction which is more complex than indicated above, *see* Erlenmeyer (Annalen, 1893, 275, 1, 13); and Erlenmeyer and Kunlin (*ibid.* 1899, 307, 146).

For the preparation of synthetic phenylalanine Fischer's method is the most practical (Ber. 1904, 37, 3062). It consists in the preparation of the corresponding bromo-fatty acid starting with ethyl malonate and benzyl chloride, and treating this with ammonia—

$$(CO_2Et)_2CH_2 \rightarrow (CO_2Et)_2CH{\cdot}CH_2{\cdot}C_6H_5$$
$$\rightarrow (CO_2H)_2CH{\cdot}CH_2{\cdot}C_6H_5$$
$$\rightarrow (CO_2H)_2CBr{\cdot}CH_2{\cdot}C_6H_5$$
$$\rightarrow CO_2H{\cdot}CHBr{\cdot}CH_2{\cdot}C_6H_5$$
$$\rightarrow CO_2H{\cdot}CH(NH_2)CH_2{\cdot}C_6H_5.$$

For other methods of synthesis, *see* Sörensen (Zeitsch. physiol. Chem. 1905, 44, 448); Wheeler and Hoffman (Amer. Chem. J. 1911, 45, 368).

The phenylalanine obtained by any of the synthetic processes described above is the racemic (*dl*-) form, it can be resolved into its optically active isomerides by the fractional crystallisation of the cinchonine salt of the benzoyl derivative (Fischer and Mouneyrat, Ber. 1900, 33, 2383), or the brucine salt of the formyl derivative (Fischer and Schoeller, Annalen, 1907, 357, 1). *d*-Phenylalanine can be obtained by the selective action of yeast in a sucrose solution on *dl*-phenylalanine (Ehrlich, Biochem. Zeitsch. 1908, 8, 438).

***l*-Phenylalanine** crystallises in anhydrous shining plates or hydrated needles containing 4 p.c. water (Schulze and Winterstein, *l.c.*), soluble in 32·4 parts of water at 25°, m.p. 278° (corr.) with decomposition, $[\alpha]_D^{20}$ −35·1°, and has a slightly bitter taste (Fischer and Schoeller, *l.c.*). The *copper salt* $(C_9H_{10}O_2N)_2Cu$ is almost insoluble in water; the *hydrochloride*

$$C_9H_{11}O_2N,HCl$$

and hydrobromide are crystalline and stable; the *ethyl ester* $C_8H_{10}N{\cdot}CO_2Et$ is an oil and forms a crystalline hydrochloride $C_8H_{10}N{\cdot}CO_2Et,HCl$, $[\alpha]_D^{20}$ −7·6°; the *formyl* derivative forms sharp four-sided plates, m.p. 167° (corr.), and has $[\alpha]_D^{20}$ +75·2°; the *brucine* salt crystallises in warty masses from methyl alcohol; the *benzoyl* derivative is more readily soluble than that of the racemic form, and has not been obtained pure (Fischer, Mouneyrat, Schoeller, *l.c.*).

Physiological action. In the normal individual phenylalanine is completely destroyed in the system, and when administered as a food it causes no increase in the amount of aromatic substances in the urine; in certain abnormal cases (*alcaptonuria*) the phenylalanine is not completely oxidised in the system and is excreted in the form of homogentisic acid (*v.* PHENYLACETIC ACID).

d-**Phenylalanine** forms beautiful plates soluble in 35·2 parts of water at 16°, m.p. 283°–284° (corr.), with decomposition; $[\alpha]_D^{16°}+35·08°$ in 2 p.c. aqueous solution; $[\alpha]_D^{20°}+7·07$ in 3·5 p.c. solution of 18 p.c. hydrochloric acid (Fischer and Mouneyrat, *l.c.*); and has a sweet taste. The *hydrobromide* forms silky needles, the *formyl* derivative $C_{10}H_{11}O_3N$ crystallises in needles or plates $[\alpha]_D^{20}-75·43°$, soluble in 145 parts of water at 27°, and melts at 167° (corr.); the *benzoyl* derivative $C_{16}H_{15}O_3N$ forms colourless needles, m.p. 145°–146° (corr.), $[\alpha]_D^{20}-17·1°$ in 7 p.c. N/1 alkali solution, the *cinchonine salt* melts at 180°–181°; the *phenyl*isocyanate $C_{16}H_{16}O_3N_2$ has m.p. 180°–181° (corr.), $[\alpha]_D^{20°}+61·27°$ in 8 p.c. alkali solution; the *α-naphthyl*isocyanate $C_{20}H_{18}O_3N_2$ has m.p. 150°–151° (Neuberg and Rosenberg, Biochem. Zeitsch. 1907, 5, 458).

dl-**Phenylalanine** crystallises from water in short stunted prisms, from alcohol in shining plates, difficultly soluble in cold water; it melts at 263°–265° with decomposition (Erlenmeyer and Lipp, *l.c.*), or at 271°–273° (Sörensen, *l.c.*). The acidic dissociation constant is $2·5\times10^{-9}$ and the basic dissociation constant is $1·3\times10^{-12}$ (Kanitz, Pflüger's Archiv. 1907, 118, 537). The behaviour of phenylalanine on heating is characteristic, a small quantity sublimes unchanged (1·5 grms. yielded 0·06 grm. sublimate after 2½ hours at 200°/1·5–2 mm., Dakin, J. Biol. Chem. 1909, 6, 235), the remainder decomposes with evolution of carbon dioxide and water and formation of a residue of *phenyllactimide* (*v. infra*), and a distillate of *phenylethylamine* (Schulze and Barbieri, *l.c.*; Erlenmeyer and Lipp, *l.c.*). On oxidation with chromic acid mixture phenylalanine yields phenylacetaldehyde and finally benzoic acid.

In its physiological action *dl*-phenylalanine resembles the *l*- form, being completely oxidised in the organism of the normal individual, and converted into homogentisic acid in the cases of alcaptonuria, although the conversion of racemic phenylalanine is less complete than that of the *l*- form (Falta and Langstein, Zeitsch. physiol. Chem. 1903, 37, 513). After intravenous or subcutaneous injection of *dl*-phenylalanine in cats or dogs, a large amount is excreted unchanged, and part is converted into *d*-carbamido-β-phenylpropionic acid (Dakin, J. biol. Chem. 1909, 6, 203).

Derivatives of dl-*phenylalanine.* The *hydrochloride* $C_9H_{11}O_2N\cdot HCl$, the *platinichloride*

$$(C_9H_{11}O_2N)_2\cdot H_2PtCl_6,$$

the *nitrate* $C_9H_{11}O_2N\cdot HNO_3$, the *sulphate* $(C_9H_{11}O_2N)_2H_2SO_4$, the *picrate*

$$C_9H_{11}O_2N)_2C_6H_3O_7N_3$$

m.p. 173°, and *picrolonate* $C_9H_{11}O_3N\cdot C_{10}H_8O_5N_4$, m.p. 238°, are crystalline. The *copper* salt

$$(C_9H_{10}O_2N)_2Cu,2H_2O$$

is sparingly soluble in cold water, and becomes anhydrous over sulphuric acid; the *silver salt* $C_9H_{10}O_2NAg$ is sparingly soluble. The *ethyl ester* $C_8H_{10}N\cdot CO_2Et$ is a thick oil sparingly soluble in water, b.p. 143°/10 mm., sp.gr. 1·065 at 15°, forms a crystalline *picrate*, m.p. 156·5° (corr.), *hydrochloride* $C_8H_{10}N\cdot CO_2Et,HCl$, m.p. 127°, *nitrite* $C_8H_{10}N\cdot CO_2Et\cdot HNO_2$, and a *diazo derivative* (ethyl α-diazo-β-phenylpropionate)

$$C_6H_5\cdot CH_2\cdot C(N_2)CO_2Et,$$

a golden-yellow oil, b.p. 90°–94°/11 mm., sp.gr. 1·107 at 10°/4°, n_D 1·5367 at 16° (Curtius and Müller, Ber. 1904, 37, 1261). The *methyl ester* $C_8H_{10}N\cdot CO_2Me$ has b.p. 141°/12 mm., sp.gr. 1·096 at 22°/4°, n_D 1·5203 at 20°; the *hydrochloride* has m.p. 158°; the *diazo derivative* $C_6H_5\cdot CH_2\cdot C(N_2)CO_2Me$, bright orange-coloured liquid, b.p. 85°–87°/12 mm., sp.gr. 1·126 at 20°/4°, n_D 1·5435 at 26° (Curtius and Müller, *l.c.*).

dl-*α-Amino-β-phenylpropionalacetal*

$$C_6H_5\cdot CH_2\cdot CH(NH_2)CH(OEt)_2,$$

obtained by reducing the ethyl ester, has b.p. 103°–105° (corr.), 0·25 mm. or 153·5°/11 mm., sp.gr. 0·995 at 20°; n_D 1·49383 (Fischer and Kametaka, Annalen, 1909, 365, 7). The *hydrochloride* of dl-*phenylalaninechloride*

$$C_6H_5\cdot CH_2\cdot CH(NH_2\cdot HCl)COCl$$

is a colourless powder; the *amide*

$$C_6H_5\cdot CH_2\cdot CH(NH_2)CONH_2$$

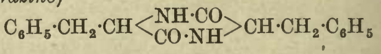
has m.p. 138°–140° (corr.), and yields the *β-naphthalenesulphonyl* derivative $C_{19}H_{18}O_3N_2S_2$, m.p. 164°–166° (corr.), and *carbethoxy*-dl-*phenylalanineamide*, m.p. 141° (corr.) (Koenigs and Mylo, Ber. 1908, 41, 4427). *Formyl*-dl-*phenylalanine* $C_{10}H_{11}O_3N$ is soluble in 240 parts of water at 27°; the *benzoyl* derivative

$$C_{16}H_{15}O_3N$$

has m.p. 187°–188° (corr.) (Fischer and Mouneyrat), its *methyl ester* $C_{16}H_{14}O_3N\cdot CH_3$ melts at 87° (corr.), and its *ethyl ester* at 95° (corr.), the *acid chloride* $C_{15}H_{14}ON\cdot COCl$ has m.p. 123°–125° with decomposition, and the *amide* $C_{15}H_{14}ON\cdot CONH_2$ melts at 198° (corr.) (Max, Annalen, 1909, 369, 276). *Phenacetyl*-dl-*phenylalanine*

$$C_6H_5\cdot CH_2\cdot CH(NH\cdot CO\cdot CH_2Ph)CO_2H,$$

m.p. 126° (Erlenmeyer and Kunlin, *l.c.*). *Phenyllactimide* (3 : 6-*dibenzyl*-2 : 5-*diketopiperazine*)



$$C_6H_5\cdot CH_2\cdot CH\genfrac{<}{>}{0pt}{}{NH\cdot CO}{CO\cdot NH}CH\cdot CH_2\cdot C_6H_5$$

has m.p. 300° (corr.) (Erlenmeyer and Lipp, *l.c.*; Curtius and Müller, *l.c.*).

*Phenyl*isocyanate of dl-*phenylalanine* has m.p. 182° (with decomp.); the *methyl*isocyanate has m.p. 176°–177°, $[\alpha]_D-14°\ 8'$ (Vallée, Ann. Chim. Phys. 1908, [viii.] 15, 331).

For a description of the preparation and properties of the chloro, bromo, iodo, nitro, and amino substituted derivatives of phenylalanine in which the substituent is in the benzene ring, *see* Wheeler and Clapp, Amer. Chem. J. 1908, 40, 337, 458; Abderhalden and Brossa, Ber. 1909, 42, 3411; Erlenmeyer and Lipp, *l.c.*;

Friedmann and Maase, Biochem. Zeitsch. 1910, 27, 97; Flatow, Zeitsch. physiol. Chem. 1910, 64, 367. Numerous *polypeptides* containing the phenylalanyl radicle are described by Leuchs and Suzuki (Ber. 1904, 37, 3306); Curtius and Müller (J. pr. Chem. 1904, [ii.] 70, 223); Fischer (Ber. 1904, 37, 3062); Fischer and Blank (Annalen, 1907, 354, 1); Fischer and Schoeller (*ibid.* 1907, 357, 1); Abderhalden and Brossa (Ber. 1909, 42, 3411). M. A. W.

PHENYLBENZYLHYDRAZINE *v.* HYDRAZINES.

PHENYLENE BLUE *v.* INDAMINES AND INDOPHENOLS.

PHENYLENE BROWN *v.* AZO- COLOURING MATTERS.

PHENYLENE DIAMINES *v.* DIAMINES.

o-**PHENYLENE DIAZO SULPHIDE** *v.* DIAZO COMPOUNDS.

PHENYLENE VIOLET *v.* INDAMINES AND INDOPHENOLS.

PHENYLGLYCINE. This compound and certain of its derivatives, more especially phenylglycine nitrile, phenylglycine-*o*-carboxylic acid and its nitrile, have during the last two decades assumed great technical importance, owing to the fact that they are all intermediate products in the manufacture of indigo by one or other of the processes based on the original synthetic method of Heumann (*cf.* INDIGO, ARTIFICIAL).

Phenylglycine, anilidoacetic acid,

$$C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}COOH,$$

may be obtained by the action of aniline on chloroacetic or bromoacetic acid (Hausdörfer, Ber. 1899, 22, 1799). The yields, however, are bad, owing to the fact that there is a tendency for two molecules of acid to condense with one of aniline. To avoid this a salt or ester of chloroacetic acid may be employed; various other processes have also been suggested.

Technical methods of preparation.

(1) Aniline is made to condense with an alkali or alkaline earth salt of chloroacetic acid (Friswell, Eng. Pat. 18149, 1907; D. R. P. 177491). The condensation is brought about in the presence of hydrated ferrous oxide or carbonate (Höchster Farbw. D. R. P. 167698). An ingenious modification of this process is to heat an aqueous solution of chloroacetic acid with nitro-benzene in the presence of finely divided iron, which first brings about the reduction of the nitro-benzene and then forms the insoluble iron salt of phenylglycine. In actual practice it is found advisable to add a small quantity of aniline to start the reaction, which takes place at 100°. When the change is complete, the mixture is distilled with steam to remove the unchanged aniline, and excess of sodium carbonate is added. The solution of the sodium salt of phenylglycine is then filtered and the phenylglycine precipitated by the addition of sulphuric acid (Höchster Farbw. D. R. P. 115797; Eng. Pat. 9700, 1906).

Amyl chloroacetate may be employed instead of the free acid to condense with aniline, and the resulting amyl ester is then saponified (Leppmann, D. R. P. 163515).

(2) Phenylglycine may also be prepared by the reduction of oxanilic acid, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}COOH$ which may be obtained in good yields by heating aniline with excess of oxalic acid. Two methods have been proposed (1) by reduction with sodium amalgam or with zinc dust (Köpp & Co., D. R. P. 163842); (2) by electrolytic reduction with lead cathodes (Kinzlberger, D. R. P. 163842).

(3) Phenylglycine is now prepared in large quantities by the saponification of its nitrile, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}CN$, which may be obtained from aniline in good yields by the action of prussic acid and formaldehyde (D. R. P. 145376).

Properties and Reactions. White crystals, m.p. 127°, moderately soluble in water, slightly so in ether, but easily so in the usual organic solvents. It forms soluble alkali salts and a green insoluble copper salt, which is an internal complex. On heating, it loses at 140° a molecule of water; on fusion with alkalis it loses water, forming indoxyl, which on oxidation in the air yields indigo; with fuming sulphuric acid it forms indigo sulphonic acid; with bromine water its aqueous solution gives a precipitate of tribromophenylglycine; with acetic anhydride it forms acetylphenylglycine.

The conversion of Phenylglycine into Indigo. The fusion with soda or potash to form indoxyl and the subsequent oxidation of this compound by atmospheric oxygen requires a temperature of over 300°, and the yields of indigo are extremely unsatisfactory; it was this fact which made the original Heumann synthesis commercially impracticable. Various condensing agents have been since proposed, and now sodamide is employed extensively and with considerable technical success, in spite of the expense of the sodamide, in the Höchster dye works.

Among other substances which have been suggested are sodium oxide mixed with soda (Basler Chemische Fabrik, D. R. P. 165691), and also calcium carbide and magnesium nitride (Höchster Farbw., D. R. P. 166213).

Derivatives.—Phenylglycine methyl ester (m.p. 48°) and *ethyl ester* (m.p. 58°) from aniline and the corresponding ester of chloroacetic acid (D. R. P. 194884).

Phenylglycine amide (m.p. 133°) from aniline and chloroacetamide.

Phenylglycine nitrile (m.p. 43°) from aniline and chloroacetonitrile, and also by the action of prussic acid and formaldehyde on aniline (Bender). On saponification it yields phenylglycine quantitatively.

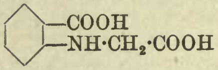
p-Hydroxyphenyglycine amide, from chloroacetamide and *p*-aminophenol, is employed as a photographic developer (D. R. P. 166799).

Nitro derivatives of phenylglycine are described by Deutsch (J. pr. Chem. 1907, [ii.] 76, 350); Borsche and Titsingh (Ber. 1907, 40, 5016); Reverdin (*ibid.* 1909, 42, 4115); Abderhalden and Blumberg (Zeitsch. physiol. Chem. 1910, 65, 318).

Phenylglycine-o-sulphonic acid, obtained by the action of formaldehyde and hydrogen cyanide on aniline-*o*-sulphonic acid (Bradshaw, Amer. Chem. J. 1906, 35, 340).

For a number of other derivatives of phenylglycine see Mauthner and Suida (Monatsh. 1890, 11, 380); Widman (Ber. 1896, 29, 1946); Fischer (*ibid.* 1899, 32, 247); Vorländer and Weissbrenner (*ibid.* 1900, 33, 555, 556); Kahn and Heimann (*ibid.* 1902, 35, 576); Schulz and Jockheim (*ibid.* 1908, 41, 3790); Leuchs and Geiger (*ibid.* 1721); Rupe and Vsétečha (Annalen, 1898, 301, 75); Rupe, Heberlien and Roesler (*ibid.* 79); Fischer and Schmidlin (*ibid.* 1905, 340, 190); Pickard (Chem. Soc. Trans. 1902, 1574); de Moulpied (*ibid.* 1905, 438); Lumière and Barbier (Bull. Soc. Chim. 1906, [iii.] 38, 123); Eng. Pat. 5763, 1900.

Phenylglycine-*o*-carboxylic acid



is an important intermediate product in the manufacture of indigo. It is obtained by the condensation of anthranilic acid and chloroacetic acid; as in the case of phenylglycine, the yields are bad, but on working with the sodium salts in aqueous solution at a temperature of 40°, the reaction proceeds smoothly owing to the fact that the sodium salt of the acid crystallises out and is thus protected from further action. Various other methods have been suggested for the preparation of phenylglycine-*o*-carboxylic acid; by heating anthranilic acid or its salts with carbohydrates such as starch or mannite or with glycerol (Badische Anilin und Soda Fabrik, D. R. P. 111067); by heating glycine with *o*-chlorobenzoic acid in the presence of copper salts, which act as catalysts (Cie. Paris. Coul. d'Anilin, Fr. Pat. 306302); by the formation and subsequent saponification of ω-cyanomethylanthranilic acid (exonitrile of phenylglycine); by the action of formaldehyde and prussic acid on anthranilic acid (*cf.* phenylglycine nitrile). This method is used extensively, and is the subject of various patents (Farbw. Mühlhem. D. R. P. 117924; Badische Anilin und Soda Fabrik, D. R. P. 216748).

Properties and Reactions. White crystals, m.p. 215° (decomp.); soluble in hot water, alcohol, ether, or acetic acid, but almost insoluble in benzene or chloroform. On heating with water it loses carbon dioxide and forms phenylglycine; on fusion with alkalis it first gives the salt of indoxylcarboxylic acid and then indoxyl, which in the presence of air is oxidised to indigo (Badische Anilin und Soda Fabrik, D. R. P. 111067); on heating with sodium acetate and acetic anhydride it forms diacetyl indoxyl (Bayer and Co., D. R. P. 85071); with fuming sulphuric acid it forms indigosulphonic acids.

Derivatives.—Phenylglycine-*o*-carboxylic acid being a dibasic acid, forms two series of mono esters, two nitriles, &c.

Dimethyl and diethyl esters, from the esters of chloroacetic acid and anthranilic acid (Höchster Farbw. D. R. P. 111911); also from the acid itself and alcohol (D. R. P. 120138).

Exonitrile (*v.* above).—Its acetyl derivative is obtained by the oxidation of acetyl-*o*-tolylglycine (Bayer and Co., D. R. P. 102892).

Halogen derivatives of phenylglycine-*o*-carboxylic acid are readily obtained by the action of halogens on the acid suspended in glacial acetic acid (D. R. PP. 148615, 158089, 216266).

Nitro derivatives of the acid are described by Purgotti and Lunnine (Gazz. chim. ital. 1903, 33, [ii.] 324), Schwarz (Monatsh. 1905, 26, 1253). *Nitroso* derivatives, which are also used in the production of indigo, have been prepared by Vorländer (Ber. 1901, 34, 164; D. R. P. 127577).

Some other derivative of the acid and esters are described in D. R. PP. 138207, 141698, 147633; also by Lumière and Perrin (Bull. Soc. Chim. 1903, [iii.] 30, 966); Villiger (Ber. 1909, 42, 3541); also by Vorländer and Mumme (Ber. 1902, 35, 1699; D. R. PP. 216748; 220839).

PHENYLHYDRAZINE *v.* Hydrazines.

PHENYLHYDRAZINE ACETYL *v.* Pyrodine.

PHENYLHYDRAZINE-*p*-SULPHONIC ACID *v.* Hydrazines.

PHENYLHYDRAZONES *v.* Hydrazones.

PHENYL HYDROGEN SULPHATE *v.* Phenol and its homologues.

PHENYL-ORTHO-OXALATE *v.* Aurin.

PHENYLOSAZONES *v.* Hydrazones.

PHENYLPARACONIC ACID *v.* Lactones.

PHESIN. A sulpho derivative of phenacetin $C_6H_3(O{\cdot}C_2H_5)(SO_3Na)(NH{\cdot}CO{\cdot}CH_3)$ used as an antipyretic. Is a light-brown amorphous powder, soluble in water, giving a Bismarck brown solution (*v.* Synthetic drugs).

PHILADELPHIA YELLOW G *Chrysaniline* *v.* Acridine dyestuffs.

PHLOGOPITE *v.* Mica.

PHLORIDZIN *v.* Glucosides.

PHLOROGLUCINOL *v.* Phenol and its homologues.

PHLOROL. The name originally given by Hlasiwetz (Annalen, 1857, 102, 166) to the homologue of phenol obtained by the dry distillation of barium phloretate, and shown by Oliveri (Gazz. chim. ital. 1883, 13, 264) to be identical with *o*-ethylphenol. The term is also applied to the mixture of xylenols that occur with creosol in the fraction of creosote of b.p. 217°–220° (Marasse, Annalen, 1869, 152, 75).

PHLOSCEÏNE *v.* Triphenylmethane colouring matters.

PHOCENIC ACID. A name given by Chevreul to *iso*valeric acid.

PHŒNICITE. *Basic lead chromate* (*v.* Chromium).

PHŒNIN and **PHŒNICEIN.** Phœnin $C_{14}H_{16}O_7$, the glucoside of the leuco compound of phœnicein, is found in the bark parenchyma cells of the *Copaifera bracteata* (Benth.) (purple wood), and crystallises from water in minute colourless needles or rods, which, on standing in air, develop a faintly violet tint. By boiling with methyl alcohol and hydrochloric acid phœnin is converted into phœnicein, and on addition of water to the acid solution is deposited as a red powder soluble in ammonia, with a violet-blue colouration. Purple wood yields approximately 2 p.c. of phœniccin.

A. G. P.

PHŒNIX POWDER *v.* Explosives.

PHONOLITH. A mixture of sanidine and nepheline, containing about 9 p.c. of potash. Used as a fertiliser (Krische, Chem Zeit. 1910, 34, 387).

PHOSGENE GAS. J. Davy's name for carbonyl dichloride or carbon oxychloride, *v.* Carbon.

PHOSGENITE. A lead chloro-carbonate $PbCl_2{\cdot}PbCO_3$, *v.* Lead.

PHOSOT *v.* Synthetic drugs.

PHOSPHINE. A syn. for phosphoretted hydrogen PH_3, *v.* Phosphorus. Used also to designate the nitrate of chrysaniline or diaminophenylacridine $C_{19}H_{15}N_3\cdot HNO_3$, *v.* CHRYSANILINE.

PHOSPHOMOLYBDIC ACID *v.* MOLYBDENUM.

PHOSPHOR BRONZE *v.* TIN.

PHOSPHORITE and **ROCK-PHOSPHATE.** General terms applied to compact or indistinctly crystallised forms of calcium phosphate, of varying degrees of purity, which are often regarded as massive varieties of the mineral apatite (*q.v.*). It is probable, however, that several allied mineral species are represented, and that the material is usually a mixture of these, together with various impurities. The materials are, in fact, more of the nature of rocks rather than simple minerals.

The term phosphorite, first used by R. Kirwan in 1794 as a synonym of apatite, is more properly restricted to the concretionary and stalactitic masses with a mamillated form externally and often a minutely radio-fibrous or convoluted structure internally. Such material, although often containing calcium fluoride in addition to calcium phosphate, differs from crystallised apatite in containing a small proportion of calcium carbonate and water. Phosphorite is generally found filling pockets or veins in limestone; for example, in Estremadura and Quercy; and in the Pacific and West Indian islands it has obviously been formed by the action of phosphatic solutions, leached from guano, on the underlying coral-limestone.

A. Lacroix (Compt. rend. 1910, 150, 1213, 1388; Minéralogie de la France, 1910, 4, 555, from a microscopical study of the French phosphorites, separates them from apatite, and places them in a separate division of his classification comprising combinations of phosphates and carbonates. In this division he recognises as species :—

Dahllite, $2Ca_3(PO_4)_2\cdot CaCO_3\cdot \frac{1}{2}H_2O$.

Francolite (and its fibrous variety staffelite, or 'hydroapatite'),

$$(CaF)_2Ca_8(PO_4)_6\cdot CaCO_3\cdot H_2O.$$

$$\text{Collophanite}\begin{cases} x[Ca_3(PO_4)_2]\cdot yCaCO_3\cdot zH_2O. \\ x(CaF)_2Ca_8(PO_4)_6\cdot yCaCO_3\cdot zH_2O. \end{cases}$$

The fibres of both dahllite and staffelite are optically uniaxial (or nearly so), with a negative birefringence a little greater than that of apatite. Collophanite is amorphous (colloidal) and optically isotropic; and with its vitreous to resinous lustre and conchoidal fracture resembles opal or gum in appearance. Only exceptionally, however, do any of these minerals occur alone in the French phosphorites; as a rule, they form interbanded mixtures, so intimately that a mechanical separation of them is impossible. For this type of mixed phosphorite the name *quercyite* is proposed; quercyite-α when the crystalline element is optically negative, and quercyite-β when it is optically positive (the crystalline element in the latter case not corresponding with any known species).

The following analyses, by Pisani, are given by Lacroix; in these it is seen that the differences in composition are only slight. I. Dahllite from Mouillac, Tarn-et-Garonne. II. Collophanite from Pouzillac, Gard. III. Quercyite-α from Mouillac, Tarn-et-Garonne. IV. Quercyite-β from Mouillac. V. Quercyite from Castillo de Belmez, prov. Cordova, Spain.

	I.	II.[1]	III.	IV.	V.
P_2O_5 .	38·40	37·40	37·60	36·60	37·75
CaO . .	53·65	49·73	51·85	50·45	52·50
F . .	(2)	0·88	1·50	0·83	(2)
CO_2 . .	5·30	3·75	4·00	4·62	5·70
H_2O . .	2·10	7·05	4·80	6·00	3·20
Fe_2O_3,Al_2O_3	0·57	0·50	—	1·30	0·85
	100·02	99·61	99·75	99·80	100·00
Sp.gr.	2·97	2·69–2·77	2·83–2·87	—	—

In the rock-phosphates occurring as nodules, pebbles, and coprolites in sedimentary rocks, or simply as impregnations of phosphatic material in the rocks themselves, the mineralogical identity of the material is still less definite. For details of occurrence and production, *see* the article FERTILISERS.

Ref.—G. P. Merrill, The Non-metallic Minerals, 2nd ed., New York, 1910. O. Stutzer, Die wichtigsten Lagerstätten der 'Nicht-Erze,' 1911, i. 265–462. X. Stainier, Bibliographie générale des gisements de phosphates, 2nd ed., Annales des Mines de Belgique, vii., 1902 *et seq.* F. Wyatt, The Phosphates of America, 5th ed., New York, 1894. A Deckers, Étude complète sur les phosphates, Liége, 1894. J. J. H. Teall, The Natural History of Phosphate Deposits, Proc. Geol. Assoc. 1900, 16, 369.

L. J. S.

PHOSPHORUS. Sym. P. At.w. 31·04. Vapour density = 61·92. From φῶς, light; and φέρω, I bear. Phosphorus was accidentally discovered by an alchemist named Brandt, of Hamburg, while experimenting with urine, in the year 1669. As urine contains only a small quantity of phosphoric acid, phosphorus was not generally known till about 100 years after, when Gahn in 1769 showed it to be an essential constituent of bones, and Scheele, taking advantage of this discovery, made phosphorus from bone ash. It is stated ' that Brandt by a secret process [3] succeeded in preparing phosphorus from urine, and he is said to have sold the secret of the manufacture to Krafft, from whom it appears that Kunkel learnt what he knew, and published in the year 1678 a pamphlet on this remarkable product. In those early days phosphorus was a very costly body, being valued as one of the most remarkable and interesting of chemical substances. Krafft exhibited it as one of the wonders of nature to various crowned heads, among others, in the year 1667, to King Charles II. of England.

From the fact of the presence of phosphorus in bones, its universal diffusion in nature might have been suspected. In fact, upon a soil free from phosphorus no plant could grow, as its presence is essential to the formation of the plant structure, and is found in largest quantities in the seed and fruit. Phosphorus, likewise, is necessary for the growth and nutrition of the animal tissues, and is present both in the substance of the brain and in the nervous matter connected therewith. It ranks, therefore, like oxygen, nitrogen, hydrogen, carbon, &c., as one of the elements necessary to the building up of the animal and vegetable body. Besides being present in all fruitful soils, phosphorus is found in most springs, in all rivers, in the sea, and even, it is stated, in minute traces in the atmosphere (Barral). At one time phosphorus was considered to be a compound body containing ‘phlogiston’ and an acid, till Lavoisier investigated the subject in the year 1780, and showed that when phosphorus is burnt in air the acid produced weighed more than the phosphorus itself, the increase in weight being due to the oxygen of the atmosphere with which the phosphorus had combined (Opuscules Physiques et Chimiques, 1774).

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[1] Also Na_2O,K_2O, 0·30.

[2] A little fluorine included with the Fe_2O_3,Al_2O_3.

[3] The process consisted in distilling evaporated urine with sand in clay retorts.

Up to the year 1845 the ‘yellow’ or ordinary phosphorus was the only variety known. ‘Red’ or ‘amorphous’ phosphorus was discovered by Schrötter in 1845, although its existence had been previously observed by other chemists, who had misunderstood its nature. Other modifications of phosphorus will be referred to when discussing the general properties of the element.

Scheele's method of producing phosphorus, first published in ‘Gazette Salutaire de Bouillon’ in the year 1775, consisted in dissolving bone ash in nitric acid, and then removing the lime as sulphate with sulphuric acid; but this method was afterwards simplified by Nicholas and Pelletier, who decomposed the bone ash direct by sulphuric acid, and further improved by Fourcroy and Vauquelin, who determined the exact quantity of sulphuric acid required for the complete decomposition of bone ash.

THE MANUFACTURE OF PHOSPHORUS.

(*a*) *The Raw Materials.—Phosphates.* Of all the phosphates now to be had in the market pure bone ash is to be preferred, other things being equal, inasmuch as it contains a high percentage of calcium phosphate; it is easily decomposed by sulphuric acid; and it contains only small quantities of magnesia, oxide of iron, and silicious matter.

On the other hand, it has to be considered that bone ash probably costs more to-day, per unit, than any other form of calcium phosphate.

Pure bone ash (from ox-bone) possesses the following composition:—

	Per cent.
Phosphoric oxide	39·55
Lime	52·46
Magnesia	1·02
Ferric oxide	0·17
Carbon dioxide, alkalis, &c. .	4·43
Water, carbonaceous matter, &c.	0·86
Silicious matter	0·51
	99·00

Bone ash, as met with in commerce, varies considerably in composition, the amount of phosphoric acid existing as tri-calcium phosphate ranging between 27 and 37 p.c. It is chiefly imported from South America, and is not obtained entirely from bones, but contains in addition the ash of other parts of the carcase. Subjoined is an analysis of commercial bone ash:—

Bone ash from South America.

	Per cent.
Phosphoric oxide	33·68
Lime	43·37
Magnesia	1·14
Ferric oxide	0·58
Carbon dioxide	4·22
Alkalis	0·62
Water, carbonaceous matter, &c.	6·70
Silicious matter	9·69
	100·00

Another very suitable calcium phosphate, which is to be had in small quantities, is what is known as precipitated phosphate of lime. This substance is obtained as a by-product in the manufacture of glue from bones. The method adopted is a modification of the system proposed by Fleck (Wagner's Chemical Technology, p. 543). The bones, previously crushed and deprived by boiling of the fat they contain, are soaked in a weak solution of hydrochloric acid, until they become quite soft. The clear liquor, containing the calcium phosphate in solution, is drawn off from the cartilaginous substance, and milk of lime is cautiously added to it, in quantity sufficient to throw down the phosphates, which are then washed, dried, and collected. The following analysis of a quantity of this phosphate which was used in the manufacture of phosphorus will show what a very rich phosphate is obtained in this way:—

Precipitated Phosphate of Lime.

	Per cent.
Phosphoric oxide	39·45
Lime	44·88

This phosphate dissolves easily and gives an excellent phosphoric acid.

The next raw material to be referred to as a source of phosphorus is apatite. Apatite is a pure form of mineral calcium phosphate, combined with either calcium fluoride or calcium chloride forming the definite chemical compounds *fluor apatite* ($3Ca_3(PO_4)_2{\cdot}CaF_2$ or *chlor apatite* ($3Ca_3(PO_4)_2{\cdot}CaCl_2$). The pure crystals of the former contain 42·26 p.c. phosphoric oxide, while the crystals of the latter contain 40·92 p.c. This last variety is not so largely imported. Fluor apatite comes from Canada, and also from Spain under the name of Spanish phosphorite. The Canadian phosphates are frequently highly crystalline and of a light green or red colour. They are found in the Ottawa district of Canada, in the volcanic rocks of New Jersey and New York, and other places in the American continent. They contain neither organic nodules nor fossils, as many other phosphates do, but have the phosphoric acid evenly distributed through large masses of the rock. The following analyses of two lots of Canadian phosphates will give some indication of their general composition:—

Canadian Calcium Phosphate.

	Per cent.	Per cent.
Phosphoric oxide . . .	33·51	37·68
Lime	46·14	51·04
Ferric oxide, Alumina Fluorine, &c. . . .	7·83	6·88
Silicious matter . . .	11·90	4·29
Water and loss on ignition .	0·62	0·11
	100·00	100·00

The absence of carbonates makes the complete decomposition of this phosphate with sulphuric acid troublesome and tedious when operating on large quantities.

The Spanish variety of apatite, called also *Estramadurite*, has the following percentage composition :—

Spanish Phosphorite (Voelker).

	Per cent.
Phosphoric oxide	33·38
Lime	47·16
Magnesia	trace.
Carbon dioxide	4·10
Sulphuric oxide	0·57
Ferric oxide	2·59
Alumina	0·89
Fluorine	4·01
Silicious matter	3·71
Water	3·59
	100·00

Another phosphate used in the manufacture of phosphorus and found very suitable, both on account of its comparative freedom from iron and the presence of a certain amount of carbonates, is 'Sombrero phosphate,' obtained from the small uninhabited island of that name in the Caribbean Sea. It contains the following :—

Sombrero Phosphate.

	Per cent.
Phosphoric oxide	35·12
Lime	51·33
Ferric oxide and alumina	1·02
Carbon dioxide	7·40
Silica	2·02
Alkaline salts	0·42
Water and loss on ignition	2·69
	100·00

French phosphates contain from 50 to 75 p.c. of calcium phosphate. The high-class qualities should be found useful in this manufacture. The next phosphate to be referred to is 'Redonda phosphate,' both on account of its high percentage of phosphoric oxide, its low price, and also from the fact that this peculiar mineral has been the subject of many patents having for their object the utilisation of the phosphoric oxide it contains. Redonda phosphate, like Sombrero phosphate, comes from the West Indies; it contains no lime, the phosphoric oxide present being combined with iron and aluminium.

Redonda Phosphates

	I.	II. (Readman)
Phosphoric oxide	35·47	39·71
Ferric oxide	8·85	9·45
Alumina	20·17	20·90
Silicious matter	9·70	6·65
Organic matter, and water of combination	7·20	22·86
Moisture	18·61	
	100·00	99·57

The processes proposed for working this phosphate will be referred to subsequently. The last mineral phosphate to be mentioned in connection with this part of the subject is what is known in the market as Charleston phosphate. This is not a high-class phosphate, like some of those considered, nor is it very free from iron and aluminium, but it has the property of being easily and uniformly decomposed when treated with sulphuric acid. and is of very regular composition. Charleston phosphate is found in the beds of several of the rivers and on the lands of South Carolina. The river phosphate differs slightly from that of the land both in colour and hardness; moreover, in the river phosphate the iron exists partly as pyrites, while in the land phosphate it exists as ferric oxide. The river variety is that usually sent to this country, being richer in phosphates. It is obtained by dredging the river, and is dried by hot air before exportation.

Charleston Phosphate (Readman).

	Per cent.
Phosphoric oxide	27·17
Sulphuric oxide	3·30
Carbon dioxide	4·96
Lime	44·03
Magnesia	0·37
Alumina	1·44
Ferric oxide	0·43
Ferric sulphide	3·60
Alkaline salts	0·87
Fluorine, &c.	2·38
Combined water and loss on ignition	4·60
Sand	5·60
Moisture	1·25
	100·00

This enumeration does not by any means exhaust the various phosphates available for the production of phosphorus; but the list here given of crude materials which are, or which may be, employed in the manufacture, will convey an idea of the resources at the disposal of phosphorus makers.

It may be added that whichever variety of phosphatic material be employed, it is absolutely essential to reduce it to a very fine state of division as a preliminary step in the manufacture of phosphorus.

Further, it must be remembered that the presence of iron, alumina, magnesia, and alkalis—as also any *excessive* amount of carbonates—is objectionable. The former substances are dissolved, to a great extent, during the sulphuric acid treatment, and reappear at a later stage, in the phosphorus retorts, while carbonates, of course, consume their equivalent quantity of sulphuric acid, and thus add to the cost of production.

As has been indicated, however, a certain limited quantity of calcium carbonate is advantageous in the sulphuric acid treatment, as it materially assists the decomposition of the phosphatic material operated upon.

The amount of calcium carbonate should not exceed, say, 10 to 12 p.c. for economical work.

Generally speaking, a high-class phosphate should be selected—one containing at least 70 p.c. of calcium phosphate. Such phosphates are now easily obtained in the market, and the advantages of employing them are very great.

With respect to the other material used in the manufacture of phosphorus (at least in the initial stage,)—namely, sulphuric acid—it will suffice to say that ordinary chamber vitriol of sp.gr. 1·500 to 1·600, free from arsenic, is quite suitable for decomposing the calcium phosphate into calcium sulphate and phosphoric acid.

(*b*) *The preparation of phosphoric acid.* In this, as in subsequent processes, the author will describe the plant (alluding incidentally to noteworthy matters) which, from personal practical experience, he has found to yield good results.

The decomposition of calcium phosphate by sulphuric acid is performed in a circular wooden vessel, shaped like a brewer's mash tun, 10 ft. in diameter and 8 ft. deep, provided with an upright wooden agitating shaft carrying three arms placed at regular intervals between the bottom and middle of the vessel.

The only ironwork in the interior of the decomposing vessel consists of a cast-iron shod on the lower extremity of the revolving shaft, and a strong cast footstep in which it works. The revolving arms are simply tenoned into the upright shaft. Pitch pine 3 ins. thick is preferably employed in the construction of the decomposer, and before use the tun is thoroughly saturated with light tar-oil, which acts as a preservative and keeps the vessel in good repair for many years. It is securely bound by strong hoop iron, which may with advantage be protected by sheet lead at any part exposed to the drip of acid. The agitator is driven by a crown wheel and pinion, connected in the usual way with a steam engine. At the lower circumference of the tun, as near the bottom as possible, a wooden man-hole door is provided, and this, opening outwards, allows the charge to be run out to the adjoining filters.

The operation of decomposing the calcium phosphate is thus conducted. The tun is filled to the depth of about 18 ins. with weak liquors from a previous decomposition, and to this is added about 2 cwts. of calcium phosphate. High pressure steam is then blown in by a lead pipe, until the liquor boils, when the steam is shut off. The agitator is now put in motion, and charging is commenced, adding alternately, say, 6 cwts. of finely-ground phosphate, and 5 carboys of chamber sulphuric acid (sp.gr. 1·500 to 1·600), till the whole has been introduced. A convenient charge for such a decomposer as has been described is from 80 cwts. to 100 cwts. of phosphate, and the equivalent quantity of sulphuric acid necessary to decompose into sulphate the *total lime present*, existing either as carbonate or as phosphate,[1] thus:

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4.$$

It is advisable not to introduce the charge too rapidly, but rather to allow ample time for a uniform decomposition to take place. The charging should be completed in three hours. and it is well to continue the agitation an hour, or even more, until all visible action has ceased.

When it is ascertained that the decomposition is complete, the large man-hole door is gradually opened, and the entire contents of the tun run off by a shoot to one of a series of filters, conveniently arranged below the level of the decomposer, agitation being still maintained.

The filters are rectangular wooden tanks, each about 20 ft. long, 16 ft. wide, and 2½ ft. deep. They are not set level, but are laterally inclined at a gradient of about 1 in 30, so as to drain towards ten exit holes pierced along the lower side. The filtering medium consists of ashes. Coarse 'clinkers' are spread evenly over the floor and a layer of sieved ashes above, the entire depth of the filtering bed being about 6 ins.

The filtering tanks are securely bound with tie rods, and before use the woodwork is impregnated with light tar-oil. As it drains from the filters, the phosphoric acid liquor is caught in a wooden launder, common to the series of outlets on the filter tanks, and is conveyed by it to wooden lead-lined tanks in which strong liquors and weak washings are kept apart.

The strength of the solution at first draining from the filters is about 30°Twad. (sp.gr. 1·150). The flow must not be allowed to proceed too rapidly, as if the bed of gypsum or 'sludge' in the filters is allowed to dry it will crack on the surface, and a very imperfect washing will be the result. A spray of water is run over the gypsum by a perforated pipe running along the higher side of the filter tanks. This spray is so regulated as to keep the sludge covered with 1 or 2 ins. of water until the end of the operation. The upper surface of the gypsum is carefully raked every few hours with a wooden mud-rake, so as to fill up any cracks through which the washing water might find too ready an exit. The spray is continued until the effluent washings are 2°Twad. (sp.gr. 1·010). The water is then turned off, and the sludge is allowed to dry, being finally piled up to permit the last trace of washings to drain from it. The gypsum is then removed from the filter tank to undergo artificial desiccation.

The phosphoric acid draining from the filters is considered 'strong liquor' until it falls below 10°Twad. (sp.gr. 1·050), and this first fraction is reserved for concentration. The latter fraction, between 10°Twad. and 2°Twad. (sp.gr. 1·050 and 1·010), is employed partly for the decomposition of a further lot of phosphate, as has been described, and partly for the first washing upon the filter before the water spray is turned on. Both fractions are blown by means of Körting's or other elevator, such as an 'acid egg,' to stock tanks, from which the evaporating vessels, and the decomposer or filters, can respectively be supplied by gravitation.

(*c*) *Utilisation of the gypsum sludge.* The wet sludge removed from the filters contains water, phosphoric acid, and undecomposed calcium phosphate in quantities varying according to the care bestowed on the operations described. The sludge may be dried upon a bed formed of fireclay-covers over flues heated by any available waste heat. When sufficiently dry, the gypsum is passed through a sieve to break up the larger lumps, and is in this state sold to manure makers as a dryer for superphosphates; or it is used to fix the ammonia in the compost heaps of the farmer, and for other purposes.

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[1] This statement differs from that given in most of the text books on Chemistry, which state that sulphuric acid is added in quantity only sufficient to form the acid calcium phosphate, thus:—

$$Ca_3(PO_4)_2+2H_2SO_4=2CaSO_4+CaH_4(PO_4)_2.$$

(*d*) *Concentration of phosphoric acid liquor from the filters.* This may be accomplished either in shallow rectangular wooden tanks, lined with 10 lbs. lead, and provided with lead pipes (1½ in. diameter, and 20 lbs. lead to 1 ft.) through which high-pressure steam is allowed to pass; or it may be performed in a cast-iron saucer-shaped pan, also lined with lead and having steam coils as before. During evaporation the liquor is maintained in motion by an agitator, provided with arms, and driven as usual by power. The latter system is the one to be preferred. Agitation of the liquor during concentration, besides hastening the evaporation, prevents the accumulation of gypsum on the steam coils, a result which invariably occurs in any unstirred evaporator. Such deposit, if allowed to form, becomes extremely hard and difficult to remove without injury to the lead pipes.

The stronger phosphoric acid from the filters —that above 10°Twad.—is allowed to flow by gravitation from the stock tank to the evaporator, to be concentrated till the clear yellow-coloured phosphoric acid attains a strength of from 65°Twad. to 100°Twad. (sp.gr. 1·325 to 1·500), according—as will be immediately explained—to the selected method of subsequent treatment. During the evaporation nearly all the calcium sulphate held in solution is precipitated, so that the concentrated acid liquor retains only a very small quantity of lime. Almost all of this lime ultimately deposits as sulphate after settling in the stock tank. As the phosphoric acid liquor becomes more and more concentrated, some of the free sulphuric acid which may be present is expelled during the evaporation—the steam or vapour from the evaporator having frequently a strong acid reaction. The following are some analyses of phosphoric acid liquors at various strengths made from phosphates which are not named:—

—	Strength				
	58°T.	69°T.	72°T.	86°T.	90°T.
Uncombined phosphoric acid (P_2O_5) .	19·30	27·60	29·20	34·02	36·44
Combined phosphoric acid (P_2O_5) .	4·68	3·61	3·60	4·40	4·80
Sulphuric acid (SO_3)	2·47	1·40	0·70	—	1·39
Alumina and ferric oxide, &c. . .	1·92	2·56	—	3·26	3·61
Lime	—	1·00	—	0·84	trace
Water	71·63	63·83	66·50	57·48	53·76
	100·00	100·00	100·00	100·00	100·00

The gypsum deposited in the evaporators or in the stock tank may either be washed by itself on a small filter, or it may be removed to the large acid filter, and be washed along with the sludge from the decomposer. If conveniently situated, the latter is the more economical method.

The concentrated acid is cooled in lead-lined store tanks, where, as has been said, the last traces of calcium sulphate are deposited, and the acid is then ready for the next operation of mixing with carbon and drying.

(*e*) *Mixture for the retorts.* The concentrated phosphoric acid may now be mixed with coarsely-ground wood charcoal, coke, or sawdust, and carefully dried in a cast-iron pot or muffle furnace. Sawdust absorbs a large quantity of liquor, so that when it is employed concentration of the acid liquor to the minimum sp.gr. of 1·320 is permissible, and, when thus saturated, it can be easily handled without loss through sweating.

On the other hand, its greater bulk and low specific gravity present objectionable features. If sawdust be employed, the mixing may be accomplished on a clean brick or asphalt floor and the wet charge can then be carefully charred in a well-built muffle furnace.

If coke or charcoal be used, the preliminary concentration of the phosphoric acid to a syrupy consistence is indispensable, and the mixing should be done in a cast-iron pot, in which the charge is subsequently dried by fire-heat from beneath. The amount of fixed carbon required is about 25 p.c. by weight of the concentrated acid liquor. Great care must be taken with the drying of the charge. The heat must be regular and not too high, and when it is completed the charred mass must be carefully preserved from air in malleable or cast-iron boxes provided with closely-fitting lids, and conveniently situated for the retorts.

(*f*) *The description of the clay retorts, their manufacture, and details of the clay employed.* The retorts in which the charred mixture is distilled are made of Stourbridge fireclay. The retorts are shaped much like a large bottle. The accompanying sectional sketch will show the appearance they present.

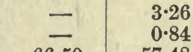

FIG. 1.—PHOSPHORUS RETORT MADE OF STOURBRIDGE CLAY.

The total length A to B is 3 ft. The internal diameter is about 8 ins. The clay is about 1 in. thick, except at B, where it is about 1½ ins. The neck is gradually tapered from C to A, where the internal diameter is 3 ins. Into this narrow orifice a 2-inch mal. iron pipe leading to the condenser is luted, and can be easily removed to empty and charge the retorts.

The retorts should be made at the phosphorus works; the clay employed is such as is used for glass-house pots, and is tolerably free from iron, rich in silica, and comparatively low in alumina. The clay, as generally supplied from Stourbridge, has previously undergone the operation of 'weathering' for many months.

This renders it plastic, more easily worked, and much more durable when made into retorts.

A mixture which has been successfully employed for the construction of retorts consists of two parts of the raw clay, finely ground, carefully mixed with one part of the calcined clay coarsely ground.

The mixture is allowed to 'sour' or season for three or four weeks by incorporating it with water to a thick doughy consistence, and leaving it piled up in a low flat heap, about 16 ft. long and 3 ft. in depth, after which it is ready for moulding into retorts. The apparatus required for the latter is not very elaborate. It consists of a turntable or wheel, upon which the retorts are built, and a sheet-iron mould about 3 ft. long, divided into two lengths of about 18 ins. each, with a fishing-rod joint to connect the one to the other.

On the turntable a loose base-piece of plank, about 12 ins. square, is first placed, to support the mould containing the soft clay retort during its removal to the drying room. Wooden beaters, and a flat circular disc, 6 ins. in diameter, with a shaft, like an old-fashioned churn stirrer, are also required.

Before commencing to build a retort, the inside of the iron mould is smeared over with oil to prevent the clay adhering to the iron. This done, the lower half of the sheet-iron mould (which is about 1 foot in diameter) is placed on the square board surmounting the turntable (a small quantity of sand having been first sprinkled over the board). The clay in a tough plastic state is introduced into the mould. This is worked by the hand to the shape of the bottom part of the retort. The clay is well beaten to the side with the wooden beater, and the bottom is pressed hard down by a circular disc. When the lower half of the retort is constructed in the way described, the upper portion of the iron mould is then jointed on, and this is likewise built up with clay in the same way until the whole retort is completed.

Some skill is required in making the tapered neck, but experienced workmen have little difficulty in doing this. The retort with the mould is now ready for removal to the stove-room, which should adjoin the retort house. The temperature in the heated room is maintained at 90°F. by means of flues below the floor. After remaining about a week in this room the retorts have shrunk sufficiently to admit of the moulds being withdrawn. When this is done, the outer skin of the retorts which was next the moulds has its hollows carefully filled up with damp clay. The retorts are then washed with a thin emulsion of clay and water until the outer surface is smooth and free from cracks or holes. They remain in this room for at least 3 weeks longer, or until they are required for use. Retorts with cracks or flaws are here rejected.

When starting a new bench of retorts, or when restarting a furnace that has been off for repairs, the retorts may be taken direct from the stovehouse and placed in the cold furnace. The fire is lighted, and the heat gradually raised to the temperature necessary for the manufacture of phosphorus.

In actual work, however, it is a common experience to find two or three retorts in a furnace broken, and, in order to replace these without interruption of the usual work, it is necessary to take the required number of new retorts from the stove-house, and place them in a special kiln, to be slowly heated to the temperature of the working furnace which contains the broken retorts. When this temperature has been attained, the new retorts are quickly removed from the kiln and are placed in the working-furnace, the broken ones having of course been first removed.

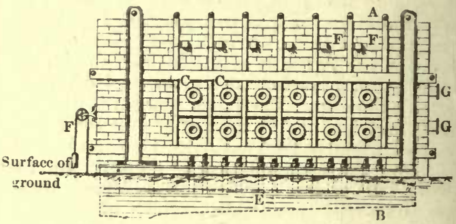

Fig. 2.—Phosphorus Furnace.

(Side elevation.)

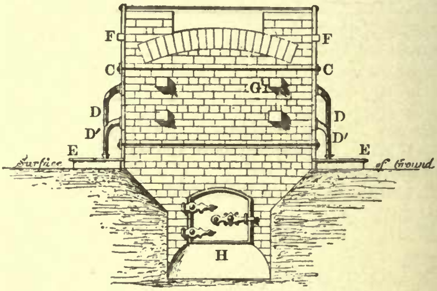

Fig. 3.—Phosphorus Furnace.

(Front elevation.)

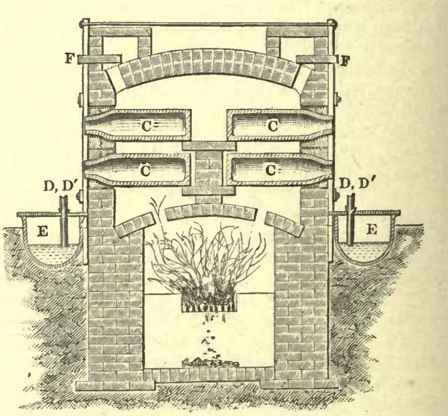

Fig. 4.—Phosphorus Furnace.

(Transverse section through A–B, Fig. 2.)

C. Phosphorus retorts. D, D′. Pipes to condenser. E. Condensing trough. F. Dampers. G. Spyholes. H. Fire door.

(*g*) *The Phosphorus Furnace.* The furnace used in the distillation of phosphorus is of the galley type, similar to that employed in the distillation of zinc by the Belgian process. A convenient size holds twenty-four retorts, twelve on each side, arranged in two tiers—that is, six retorts on each tier. The retorts are placed back to back, their necks protruding slightly (1 in.) through the side walls of the furnace. The closed ends of the retorts are supported by a 9-inch wall, having fireclay covers built into it over the spaces into which the ends of the lower tier are inserted. This wall divides the furnace longitudinally. The furnace measures about 12 to 13 ft. long and about 7 ft. broad, outside dimensions. The firegrate is 5½ ft. in length by 1½ ft. in breadth, and the firebars are made of 2-inch square wrought-iron. Over the firegrate, about 2½ ft. above the bars, a 4½-inch firebrick arch is thrown. This arch has six ports on each side, corresponding to the six retorts, and these are so placed that the fire ascends between each pair or retorts. The arch extends from end to end of the furnace. Upon the top of this arch the 9-inch wall previously mentioned is built. This wall is about 2 feet in height, and is sufficiently high to allow the ends of the upper tier of retorts to rest on the top of it, the ends of the lower tier resting on covers built into the wall about 6 ins. above the arch which covers the fire. The outer walls of the furnace are 9 ins. thick, and the outer arch which incloses the whole is also made of 9-inch firebrick. The retorts are, in fact, simply suspended in what is practically two flues in one furnace, the walls of which are the outer walls of the furnace and the 9-inch central dividing wall.

The furnace must be very firmly bound, both longitudinally and transversely. This is all the more required as the walls of the furnace must necessarily be thin, and, moreover, each retort has a 12-inch square port-hole through which it is primarily introduced into the furnace. All these circumstances, tending to weaken the side walls, point to the necessity of securely and substantially binding the furnace.

The preceding sketches (Figs. 2, 3, and 4) will show the general construction and arrangement of the furnaces and side condensing troughs.

The heat from the fire ascends through the ports of the 4½-inch arch described above, and passes through the chambers in which the 24 retorts are hung, and then it escapes through 6 ports of the upper 9-inch arch to small flues built on either side of the top of the furnace. The products of combustion now travel along these flues and descend at the back of the furnace furthest from the fire to the main flue. If required, this waste heat may be first utilised to dry the gypsum from the phosphoric acid filters. The firebricks used in the construction of the furnace must be of the very best description, and none but a most experienced furnace-builder should be intrusted with the erection of it. Dampers are placed on each of the upper port-holes, and a large damper where the two small flues unite with the main flue. Spyholes should be placed on the front wall of the furnace, so that the chambers containing the retorts can be conveniently viewed. This is a most important provision, and should in no case be neglected, as frequently retorts are cracked, and there is no other means so simple as the spyhole to ascertain their condition. When starting a new furnace great care must be taken not to raise the heat so rapidly as to cause cracks in the walls, which would admit cold air and be fatal to the retorts; and, when the necessary heat has been attained, as much caution is required to maintain a steady temperature. Clay retorts are very sensitive to sudden changes of temperature, and the life of a retort largely depends upon its treatment in this respect.

(*h*) *The Distillation.* The 24 retorts having been placed in the port-holes in the manner described, their necks are built in with broken bricks and fireclay to prevent access of air into the interior of the furnace. The fire is now lighted and the heat very gradually increased, care being taken during this time to have the dampers only slightly open. After 18–24 hours firing the retorts should be at a bright-red heat and ready for charging. This is performed by means of a scoop, made out of a 2-inch malleable iron pipe, which has been opened up and provided with a handle. The scoop is about 18 ins. long, and made so as to enter the 3-inch neck of the retort without difficulty.

The retorts hold conveniently about 20–30 lbs. of the charred mixture. It is advisable not to fill them more than two-thirds full. This does not take more than a few minutes to accomplish, and whenever it is done the 2-inch malleable iron pipe leading to the condenser should be at once luted on. Various forms of condensers may be employed. A suitable arrangement consists in having long troughs on each side of and close to the furnace (as shown in Figs. 2, 3, and 4) made of light cast-iron, about 12 ft. in length by 18 ins. broad by 24 ins. deep at one end and 18 ins. at the other end. The lip of these tanks has a 3-inch flange on the outside, upon which the cast-iron cover is bolted. Twelve 3-inch cast-iron pipes with faucets pass through this cover, and dip an inch or two into the water with which the trough is partially filled. These short pipes are so placed that the 2-inch malleable iron pipes before referred to can be conveniently luted to their faucets, and thus connect the retorts with the condenser.

The water in these troughs soon becomes warm with the hot gases bubbling through it. This is advantageous, as it prevents solid phosphorus choking up the pipes. The bottom of the troughs being deeper at the one end than at the other causes the melted phosphorus to run down to the lower end, from which it can be removed from time to time by ladles.

The incondensable gases are removed from the trough by a 10-inch pipe, and can either be sent at once to the stalk or connected with further condensing arrangements. Care must be taken when charging the retorts to avoid spilling any of the charge into the condensing troughs, and to insure this it is well during the operation to employ sheet-iron trays which cover the open faucets.

The luting used for the 2-inch pipes, both at the retort and faucet ends, is fine ground fireclay, with salt, or with a small quantity of borax added to prevent cracking. After the retorts are all charged, the heat is raised to a temperature approaching whiteness. The odour of sulphurous acid may then be detected in the escaping gases, especially if the charged mixture has not been sufficiently dried. Sulphides are next discoverable, and lastly, in about two or three hours, phosphorus. The distillation should be completed in about 16 hours, and after withdrawing the residues from the retorts and slightly cooling the furnace, the charging can be recommenced as before. Retorts, if carefully attended to, may last a considerable number of distillations.

When the temperature is fully up and phosphorus is coming off vigorously, the retorts should be examined by the spyholes, when the smallest flaw can be easily detected by the bright dazzling phosphorus flame which issues from the smallest crevice. When this is observable the retort should have its charge withdrawn, and the retort itself is then taken out and replaced by one from the kiln heated to the temperature of the phosphorus furnace, as has been already described. There is no difficulty in doing this, as the ports are intended to permit this very operation.

The chemistry of the process of preparing phosphorus from phosphoric acid may be described as follows :—The orthophosphoric acid liquor (H_3PO_4), after being mixed with carbon and heated to a dull red heat, is resolved into metaphosphoric acid (HPO_3), and when this is further heated to a high temperature in the retorts it is broken up by the carbon originally added and phosphorus distils over. The change may be thus represented :

$$4HPO_3+12C=2H_2+12CO+P_4.$$

An example of the yield, &c., from a known amount of phosphoric acid may be of interest.

Quantities taken :—

502 lbs. of phosphoric acid liquor containing 25·7 p.c. free P_2O_5.

137 lbs. of coarse wood charcoal.

These were mixed together and dried in the manner described.

The dried mixture weighed 380 lbs.

On distillation the following results were obtained :—

Residue in retorts weighed 67 lbs.

Yield of *refined* yellow phosphorus, 38 lbs.

Theoretical yield, 56·2 lbs.[1] (Yield = 67·5 p.c.)

(*i*) *The Crude Phosphorus.* The phosphorus obtained in the condensers varies very much in appearance from a pale buff to a brick-red chocolate, or nearly black, colour. The colour is no doubt due to impurities, as well as to the presence of lower oxides of phosphorus and amorphous phosphorus. If condensed in *cold* water, it resembles the raspings of cork and floats on water. The crude product is ladled out of the condensing trough into malleable iron boxes provided with handles, in which it is carried to the refinery. Phosphorus in this condition is much more inflammable than it is in a pure state, and great care must be observed in the handling of it.

(*j*) *The Refining.* There is always more or less sand and clay mingled with the crude phosphorus, partly due to the unavoidable dust in the furnace-house and also to the luting. To get rid of this, it is advisable to fuse the crude product under hot water, and, after a thorough stirring with a wooden rake, to allow the mass to solidify, when it can be easily broken up with chisels, and is then of a uniform character.

The sand, clay, &c., mixed very frequently with some phosphorus, are left on the upper surface in a loose pulverulent condition. If these impurities are found to contain phosphorus, they may be distilled in an iron retort and the phosphorus recovered.

The solidified phosphorus is now ready for refining. The method described in text-books is to squeeze the melted phosphorus through chamois leather. A more rapid method is either to distil it in an iron retort or to refine by the use of chromic acid. The last method is probably the one most to be recommended. To carry out the refining by this process the crude phosphorus is first fused under water in a small lead-lined agitating pan provided with a lead steam-coil, and from 3–4 p.c. of potassium or sodium dichromate (previously dissolved in water is added. Sulphuric acid in equivalent proportion is next run into the agitator, and the whole is left to mix for 2 hours or more. After that time the phosphorus should be of a pale-yellow colour and almost transparent. The chrome liquors are now carefully syphoned off, and the phosphorus then receives a washing with hot water, after which it is syphoned off and rapidly filtered through a canvas filter-bag to remove the mechanical impurities. The phosphorus is now ready for moulding.

(*k*) *The Moulding.* The phosphorus melted under hot water may now be cast into 'wedges,' or made into 'sticks.' The 'wedges' or 'pains' (of the French manufacturer) are easily made. The liquid phosphorus is ladled under hot water into tin moulds 10½ ins. diameter by 4½ ins. deep, standing in a row in a shallow trough, and while still liquid a star-shaped arrangement, made also of tin, is dropped into the mould. The object of this is to divide the circle equally into 10 sectors or wedges. On solidifying the phosphorus by running in cold water into the trough and then removing it from the mould, 10 separate wedges are obtained in a convenient form for packing, each wedge weighing about

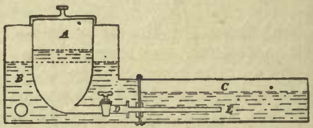

Fig. 5.—Section of Apparatus for Moulding Phosphorus into Sticks.

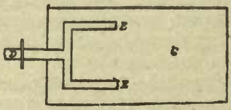

Fig. 6.—Plan of Cold Water Tank for Moulding Phosphorus into Sticks.

A. Pot for melting phosphorus under water. H. Hot water tank heated with steam coil. C. Cold water tank, flanged to B. D. Cock for escape of liquid phosphorus. E. Metal tubes. (Same letters apply to Figs. 5 and 6.)

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[1] From phosphorus in free P_2O_5.

2 lbs. To admit of easy removal of the phosphorus, the tin mould divides into 2 parts and is made tight by india-rubber joints and flanges, &c.

If the phosphorus is desired in the form of 'sticks,' the fused element is drawn through glass tubes in an apparatus illustrated by the sketches (Figs. 5 and 6).

Another method of moulding is to run the liquid phosphorus into slightly-tapered tin tubes made of a length to suit the tin packing-cases. The tubes are closed at one end by corks, and are set (corked end down) in troughs containing hot water, when the tubes are filled with the molten phosphorus. Cold water is run into the trough to solidify the latter, which is then removed from the moulds.

(*l*) *The packing.* The 'wedges' are packed along with water in tin cylinders, holding 50 kilos. of phosphorus. The dimensions of the cylinders are 22 ins. deep by 11 ins. diameter. The lids (11 ins. diameter) are loose, but fit tightly inside, and have a ¾-inch hole, through which water is poured after the lids are soldered on. These small holes are finally soldered up, and the cylinder is thus hermetically sealed and completely filled with water. Another size of case sometimes employed holds 25 kilos.; it is 12 ins. deep by 11 ins. diameter.

The tin packing cylinders should be provided with three wire handles—two opposite one another—at the upper part, and the third lower down near the base. These are found convenient in handling.

The sealed tins are now packed along with sawdust in rectangular wooden boxes 24 ins. long by 12¼ ins. broad × 12¼ ins. deep. The wood is pine ⅝ in. thick. The boxes should be strengthened with hoop-iron at the edges. The sawdust is tightly rammed down between the tin case and the side of the box, and thus makes a firm and safe package.

When exporting phosphorus to certain countries—*e.g.* Germany—the wooden boxes require to be further packed in canvas, and iron handles must be tightly fixed to either end of the box for convenience in lifting.

The 'stick' phosphorus is packed along with water in tins which hold 10 lbs. each. The tins are 7⅝ ins. long by 5⅝ ins. diameter; each one holds about 90 sticks (7½ ins. long by ½ in. diameter).

The lids, &c., are soldered on as before described. These tins are further packed as in the case of 'wedges,' in wooden boxes holding ten in a box.

(*a*) *Other proposed methods of manufacture.* (1) Donovan proposed to mix lead phosphate (obtained by acting on bones with nitric acid and then precipitating by lead acetate) with finely-divided charcoal, and to distil for phosphorus.

(2) Fleck proposed to combine the manufacture of phosphorus with that of glue and gelatin. By this method the bones, freed from fat, are decomposed with weak hydrochloric acid, which dissolves out the calcium phosphate, leaving the cartilaginous matter insoluble. The acid phosphate liquor is evaporated, mixed with carbon, and distilled in suitable retorts.

(3) E. C. Mantrand (Eng. Pat. 1166, May 25, 1854) patented a method of preparing phosphorus by decomposing an intimate mixture of calcium phosphate, carbonaceous matter, and silicious matter at a bright red or white heat in an atmosphere of hydrochloric acid or chlorine gas, when phosphorus, phosphoretted hydrogen, carbon dioxide, &c., distil over.

(4) Wöhler suggested the method of decomposing calcium phosphate with silica and carbon, and distilling.

(5)[1] Gentele, in 1857, published a plan of phosphorus manufacture combined with the preparation of sal ammoniac. He treats the bones with hydrochloric acid. To the resulting solution crude ammonium carbonate is added. The precipitated calcium phosphate so obtained is employed in the preparation of phosphorus, while the solution of ammonium chloride is evaporated and sublimed for sal ammoniac.

(6)[1] Gerland (in 1864) suggests the treatment of bones with an aqueous solution of sulphurous acid.

(7)[1] Minary and Sourdray (1865), proposed to prepare phosphorus from a mixture of iron phosphate and well-ignited coke.

Besides the above, letters patent have been taken for the following methods of preparing phosphorus:

R. Lammy (Eng. Pat. 311, 1857) grinds ammonium phosphate with carbon, dries, and distils, producing first ammonia and then phosphorus.

R. A. Brooman (Eng. Pat. 2294, 1864). Silica, iron, and coal are added to calcium phosphate in such proportion that silica can form with lime a fusible slag, and iron phosphide is obtained. This latter may then be heated to quick redness with sulphur, sulphuretted hydrogen, carbon disulphide, &c., &c., to obtain phosphorus.

J. H. Player (Eng. Pat. 660, 1866, and 1064, 1867) mixes phosphoric acid liquor evaporated to a thick paste with (1) spent tan or (2) with coal or coke in fine powder. He then carbonises to remove volatile matters, and distils the residue in clay retorts in the usual way.

E. Aubertin and L. Boblique (Eng. Pat. 2458, 1867) (1) mixes fine ground calcium phosphate with twice its weight of silica and 25 p.c. of coke, and heats to orange-red or white heat, when phosphorus comes off *without fusion.* No apparatus is described.

Claude Brison (Eng. Pat. 3515, 1868) patents the employment of a blast-furnace and blowing engine in the manufacture of phosphorus, and also the admixture in the blast-furnace of the fuel with the materials for producing the phosphorus. 'The mixture employed by preference for producing the phosphorus consists of calcium phosphate, silica, and carbonate of soda; the whole thoroughly desiccated.'

E. Aubertin (Eng. Pat. 1593, 1870) secured a further patent for producing phosphorus from calcium phosphate, silica, and carbon. *1st process:* By calcination in a furnace or retort at a temperature from 2192° to 2404°F. *2nd process:* By fusion. Apparatus in this case is by preference a 'Fluss-ofen' blast-furnace, and the temperature is 2192°–2932°F.

J. H. Player (Eng. Pat. 3501, 1872) proposes to utilise the waste gases from the retorts by passing them through a solution of copper sulphate, whereby copper phosphide is obtained.

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[1] Wagner's Chemical Technology, p. 544.

J. Townsend (Eng. Pat. 1862, 1872) distils Redonda phosphate either along with carbon and a flux of common salt or borax, or with a mixture of potassium and sodium sulphates, and so obtains phosphorus.

J. P. Serve (Eng. Pat. 49, 1879) employs a furnace—either a reverberating or blast-furnace—or retorts, and claims (1) 'the preparation, in the form of blocks or bricks, of intimate mixtures and in suitable proportions, of phosphates of lime, &c., &c., and of silica or other silicious body bound or held together by a carburetted body such as tar-pitch or coal.' (2) The extraction of the phosphorus from the blocks or bricks. (3) a special construction of blast-furnace and condensers.

A. Nicolle (Eng. Pat. 1693, 1888) decomposes mineral phosphate with nitric acid, and treats the resulting solution with potassium sulphate. He then filters from the calcium sulphate which is precipitated, and treats the filtrate with mercurous nitrate, thus obtaining mercury phosphate. This is washed, dried, and distilled with carbon, when mercury is first obtained, and then phosphorus.

J. B. Readman (Eng. Pat. 14962, 1888) claims the application of heat produced by passing an electric current through the materials containing phosphorus placed in a closed furnace.

Parker and Robinson (Eng. Pat. 17719, 1888) claim the employment of electricity on similar lines to foregoing patent.

Folie-Desjardins (Eng. Pat. 13240, 1890) for a process for the simultaneous manufacture of phosphorus and of alkaline silicate—(1) by heating a mixture of the phosphate with one or more alkaline sulphates or carbonates with or without the addition of silicic acid or a flux in a reverberatory furnace, or in retorts within a regenerative gas-furnace, lixiviating the resulting mass, and evaporating solution to obtain the alkaline phosphates; (2) heating a mixture of the alkaline phosphate so obtained with silica and carbon in retorts placed in a regenerative furnace, thereby effecting the simultaneous production of phosphorus and an alkaline silicate.

Coignet (Eng. Pat. 2970, 1891) claims improvements in the moulding of phosphorus to avoid the carriage of much water in the packing cases.

The author has conducted a large series of experiments (*v.* J. Soc. Chem. Ind., vols. 9, 10), with the view of obtaining phosphorus by distillation *direct* from the raw phosphate of lime, without the employment of sulphuric acid at all or the preparation—as an intermediate stage—of phosphoric acid. He has proved conclusively that silica in the form of sand, ganister, or flints intimately mixed with calcium phosphate and carbon, in suitable proportions, is capable, at a high temperature, of effecting the decomposition of the phosphate, expelling practically all the phosphorus contained in the mixture, leaving, as a residue, a fluid slag. Further, that with adequate condensing appliances a very large proportion of the phosphorus so expelled may be collected. Similarly, satisfactory results have been obtained by the employment of other phosphates, such as phosphate of alumina, &c., provided fluxes suitable for each case are employed.

Retorts were found unsuitable for the distillation, both on the score of economy and durability, and the blast furnace, which was tried for some time, presented many practical difficulties in its working.

The success of the application of electricity to the production of certain metals and alloys, notably those of aluminium, led him to try that source of energy for the production of phosphorus, and the result has been that the author, along with T. Parker (who applied for letters patent only a few weeks after the author's application) (Readman's patent, 14962, Oct. 18th, 1888; Parker and Robinson's patent 17719, Dec. 5th, 1888) arranged for the erection of a large experimental plant with engines, dynamos, and electric furnaces capable of turning out about 40 cwt. of phosphorus per week.

The object which has now been successfully attained in the new process, called the Readman-Parker and Robinson system, is the *continuous* production of phosphorus *direct* from raw materials by means of the electric furnace, the heat being applied in and through the phosphorus-bearing mixture in the furnace, and not, as in the case of distillation, in retorts, heated from the outside, involving, in consequence, a great expenditure of fuel.

The process is carried out as follows. The phosphate, carbon, and fluxes, in proper proportions and all carefully and intimately mixed together, are introduced (previously heated to as high a temperature as possible) into the upper part of the electric furnace by means of a tight-fitting hopper arrangement, the electric current is led to and from the furnace by copper cables connected to large carbon electrodes situated on either side of the furnace. The furnace itself is practically an iron tank, lined inside with refractory bricks, thus making a kind of brick-sided trough about 18 inches square and 36 inches deep, closed at the top by the hopper referred to, and having an outlet pipe to the condenser placed on the upper part of the side of the furnace.

After the charging of the furnace, the current is turned on, and soon indications of phosphorus may be seen in the condensers. The gases escaping by the side pipe pass on to a series of copper condensers, the first of which contains hot and the others cold water, when they are allowed to escape into the air. As the phosphorus is distilled off from the mixture the residue in the furnace forms a liquid slag, which from time to time is tapped out at the bottom of the furnace, fresh phosphorus-bearing mixture being introduced by the hopper at the top precisely as in blast-furnace practice, where closed tops are used. In this way the operation is made continuous, and is carried on for days without cessation.

The mixed materials, as introduced into the electric furnace, can be had to contain about 14 p.c. of elementary phosphorus, and as the weight of the slags from these is not so much as half the weight of the original mixture, and as, moreover, the slag on an average contains only about 1 p.c. of phosphorus, it will be apparent that the decomposition is remarkably complete.

The crude phosphorus obtained in the condensers is refined in the way previously described.

The advantages of this process may be summarised as follows. No sulphuric acid is required, no need to prepare and concentrate phosphoric acid, much less handling of materials, no fire-clay retorts employed, less loss during process, larger yields, and less consumption of coal.

THE PRODUCTION OF AMORPHOUS PHOSPHORUS.

Amorphous phosphorus in compact pieces is a reddish-brown, moderately hard substance,[1] somewhat resembling in appearance the hematite iron ore of Cumberland. It is opaque, with a slight metallic lustre. It is brittle and easily broken, and exhibits a conchoidal iron-black fracture with sharp edges.

The sp.gr. of amorphous phosphorus is 2·25. It is without taste or smell, is unattacked by most solvents, and if taken internally is excreted unchanged.

Amorphous phosphorus, as met with in commerce, frequently contains small quantities of ordinary phosphorus, from about ½ p.c. downwards according to Fresenius; in addition, it usually contains phosphoric acid, graphite, and other impurities, and has generally an acid reaction.

The following is an analysis of amorphous phosphorus :—

	Per cent. (Readman)
Phosphorus	93·44
Phosphoric acid	3·58
Ferric oxide and alumina . .	0·78
Alkalis, carbon, loss, &c. . .	0·84
Insoluble in nitric acid . . .	1·36
	100·00

Ground amorphous phosphorus dissolves very easily in nitric acid on account of its state of sub-division.

Chlorine has no action on this variety of phosphorus unless the latter is heated, when it burns with a yellow flame.

For ignition, amorphous phosphorus requires a temperature of at least 240°.

(*a*) *The apparatus and process.* The conversion of yellow into amorphous phosphorus is effected by heating the former to a temperature between 240° and 250° for some time.

The apparatus employed is a cast-iron pot which is closed with a cover. A narrow tube open at both ends is screwed into the upper part of the pot. This acts as a safety valve, and avoids all risk of explosion.[2]

If pressure be employed within the pot and the temperature exceeds 300°, the yellow is transformed into amorphous phosphorus in a very short time. There is, however, considerable danger in this treatment which might far outweigh the economy in time. According to the method used, when the conversion is effected in open iron vessels in which the air finds but limited access, the process, though tedious, is free from all difficulty or danger.

Ordinary phosphorus may also be converted into amorphous phosphorus by chemical action, as by heating it to 200° with a small quantity of iodine.

(*b*) *The refining.* The amorphous phosphorus, obtained in the cast-iron pots, is in hard compact lumps. These are ground under water, and freed from ordinary phosphorus by boiling the ground powder with a solution of caustic soda; it is then repeatedly washed with boiling water and carefully dried by steam heat.

(*c*) *The packing.* The ground red phosphorus, dried in the manner described, is sent out in the dry state in tin boxes holding 10 lbs. each.

PROPERTIES OF ORDINARY PHOSPHORUS.

Phosphorus at the ordinary temperature is a pale yellow, soft and flexible, translucent, waxy-looking solid, which becomes hard and brittle at temperature below 5·5°. It is extremely inflammable, especially if not quite pure, and must always be kept under water. It has a great affinity for the oxygen of the air, with which it combines directly.

It also combines *directly* with chlorine, bromine, iodine, and sulphur, but not with nitrogen and hydrogen.

Phosphorus is luminous in the dark, and in a moist atmosphere a gradual oxidation takes place with formation, first of phosphorous acid, and ultimately of phosphoric acid, ozone and hydrogen peroxide being likewise produced at the same time. When exposed to daylight, under water, a whitish incrustation is formed, which frequently becomes of a reddish hue. According to Baudrimont (Compt. rend. 61, 857, 1866), the crust is formed only under influence of oxygen, and possesses all the usual properties of ordinary phosphorus. Sp.gr. at 16°, 1·82.

Melting-point, under water in an open vessel, 43·3°; in closed vessel without water, phosphorus melts at 30°. In both cases, if left undisturbed in a smooth glass vessel it may remain liquid at temperatures considerably below the melting-points. It distils at 269°, the vapour being colourless, and takes fire in air when heated to 34°. It is very soluble in carbon disulphide, one part dissolving 9·26 parts of phosphorus, a slight amount of heat being developed, but on cooling to ordinary temperatures some of the phosphorus is precipitated in a crystalline form.

Phosphorus is also very soluble in sulphur chloride, phosphorus trichloride, and phosphorus sulphide. It is nearly insoluble in water.

The following table shows the weight of different solvents required to dissolve 1 part by weight of phosphorus. The temperature of the solvent, unless otherwise stated, is 12° :—

	Parts
Benzene (90 p.c. sp.gr. 0·878) . .	82·5
Chloroform	83
Aniline	154
Oil of turpentine	162
Paraffin oil (sp.gr. 0·806) . . .	179
Ethyl ether (sp.gr. 0·725) . .	203
Olive oil	649
Alcohol (sp.gr. 0·801) . . .	764
,, ,, ,, at 40° . .	535
Wood spirit (sp.gr. 0·846). . .	1408
,, ,, ,, ,, at 40° .	862
Acetone	2702
Solution of caustic soda (sp.gr. 1·35) .	194
Liquor ammoniæ (sp.gr. 0·880) .	3030

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[1] The hardness of amorphous phosphorus lies between calcareous spar and fluor spar.

[2] See Eng. Pat. 13695, by A. Albright, 1851.

The ammoniacal solution becomes dark brown, and the surface of the phosphorus is coated with a brown-black deposit. When water is added to the greater number of the above solutions, the phosphorus is precipitated.

Cold concentrated nitric acid dissolves phosphorus. If exposed to the action of dilute nitric acid for some time its crystalline character becomes evident.

Sulphuric acid (92 p.c. O.V.) does not dissolve phosphorus in the cold, but attacks it on prolonged boiling. Phosphorus is insoluble in cold concentrated hydrochloric acid.

Phosphorus fumes in the air, emitting a garlic-like odour. On exposure to air, it not unfrequently melts and takes fire, and during combustion dense white fumes of phosphoric oxide are produced, which can be collected in snowy flakes. The burns produced by ignited phosphorus are of a serious nature, and are very slow in healing, any unconsumed phosphorus left on the wound being most difficult and painful to remove.

Phosphorus sometimes contains a small proportion of arsenic derived from the sulphuric acid used in the preparation of the phosphoric acid. If this be present in any quantity the refined phosphorus has a red or mahogany colour. Phosphorus is a powerful poison; less than 2 grains are said to have caused death. Those who have to handle it frequently are liable to necrosis, which begins with the disintegration of the jaw-bones, and ends with their total destruction. Ill-fed and scrofulous persons are said to be specially affected. It is rather a curious circumstance that persons engaged in the manufacture of phosphorus do not appear to be affected by this disease.

Phosphorus does not conduct electricity (Faraday).

According to Deville and Troost, the vapour of phosphorus has a sp.gr. of 4·50 at 1040°; it is concluded, therefore, that there are four atoms in the molecule.

Phosphorus is tough, and cannot be pulverised; but if melted under water and shaken until the fluid is quite cold, it is reduced to a fine state of division in the form of round pellets of various sizes; an aqueous solution of urea or alcohol aids this formation. When heated with aqueous vapour to a temperature of 250°, phosphorus decomposes the water, phosphorous acid and phosphoretted hydrogen being formed.

Phosphorus volatilises to a small extent when boiled with water.

Phosphorus *in vacuo* volatilises at ordinary temperatures. It is not luminous in pure oxygen at temperatures below 20° (Müller); but if mixed with a neutral gas, or if it be rarefied, then luminosity is at once seen (Graham). The presence of mercuric chloride and of phenol (Polstroff and Mensching, Chem. News, 57, 71), and of certain gases, such as olefiant gas, sulphuretted hydrogen, or the vapours of turpentine or ether when present even in small quantities, prevent the glow of phosphorus. If hydrogen, nitrogen or carbon dioxide in which phosphorus has been exposed be brought into contact with oxygen it becomes luminous from the phosphorus diffused in the gas.

Phosphorus at high temperatures combines with most of the metals forming phosphides. For example, if calcium phosphate and silica with carbon and iron (as ore or metal) be heated to a high temperature, a very fusible iron phosphide, Fe_2P, can be obtained.

Phosphorus, owing to its affinity for oxygen, is a powerful reducing agent. It precipitates copper, silver, platinum, palladium, and gold when brought into a solution of the salts of these metals.

Besides the red or amorphous, there appears to be a third allotropic modification of phosphorus—viz., metallic or rhombohedral phosphorus—formed by heating the element in sealed tubes along with metallic lead for some hours. On cooling, crystals are found permeating the lead; these are separated by dilute nitric acid, which dissolves out the lead. This phosphorus is a dark crystalline substance, sp.gr. 2·34 at 15·5°.

H. M. Vernon (Phil. Mag., October 1891) states that a rhombic modification of phosphorus exists, melting at about 45·3°, and of sp.gr. 1·8272. It appears to be formed from the octahedral variety by slowly cooling it when liquid.

Uses of phosphorus and statistics of the trade. The chief consumption of phosphorus at present is in the manufacture of matches, in which it is used as phosphorus sesquisulphide. The so-called 'safety matches' which ignite on the box, have no phosphorus on the match itself, but have a thin layer of red or amorphous phosphorus on the sides of the box.

Phosphorus is used in medicine in small doses. It is likewise employed in form of a paste for the destruction of rats and mice. It is also used in the laboratory, and in the manufacture of many organic compounds.

Phosphorus as calcium phosphide is one of the constituents of the material used for distress signalling at sea.

Phosphor bronze, which is now extensively employed in the arts, contains a small percentage of phosphorus, which modifies the properties of copper to a large extent favourably when present in minute quantities, and unfavourably if present in more than 2–3 p.c.

At the present time, most of the phosphorus manufactured in Europe is made by Messrs. Albright and Wilson, Ltd., of Oldbury, Birmingham, England, Messrs. Coignet and Cie., Lyons, France, and the Chemische Fabrik Griesheim-Elektron, Frankfort-a-Main, Germany. There are also one or more makers in Russia. Canada and the United States of America are supplied by factories in each of those countries. J. B. R.

NON-METALLIC COMPOUNDS OF PHOSPHORUS.

Hydrogen phosphides. Three of these compounds, PH_3, P_2H_4, and P_4H_2(?), are known, the first being gaseous, the second liquid, at ordinary temperatures, and the last solid.

Phosphorus trihydride, phosphoretted hydrogen, or *phosphine*, PH_3, is usually obtained by heating phosphorus with milk of lime or strong potash: $3KHO+3H_2O+P_4=PH_3+3KH_2PO_2$, or by decomposing calcium phosphide with water: $3Ca_2P_2+12H_2O=4PH_3+P_2+6Ca(HO)_2$.

It is also formed by the action of dilute acids on the phosphides of zinc, iron, tin, magnesium and aluminium (Lüpke, Chem. Soc. Abstr. 1891, 397; Matignon, Compt. rend. 1900, 130, 1391). Hydrogen phosphide is also evolved when yellow phosphorus is acted on by warm water, by hydrogen peroxide, or by sodium hydroxide (Weyl, Ber. 1906, 39, 1307).

As thus prepared, the gas contains a sufficient amount of the dihydride, P_2H_4, probably produced by a secondary reaction,

$$Ca_2P_2+4H_2O=2Ca(OH)_2+P_2H_4,$$

to render it spontaneously inflammable. When the gas is passed through water, each bubble on entering the air gives rise to a vortex ring of phosphoric oxide or metaphosphoric acid. The gas also contains hydrogen produced by the gradual decomposition of the hypophosphite by the alkali: $KH_2PO_2+2KOH=2H_2+K_3PO_4$.

The spontaneous inflammability may be destroyed by decomposing or condensing the dihydride by exposure to light, or by passage through a tube cooled by a freezing mixture.

The trihydride may be obtained free from the dihydride by decomposing calcium phosphide with hydrochloric acid, which converts any dihydride formed into the gaseous and solid hydrides. It may be prepared pure by decomposing phosphonium iodide with water, or preferably with potash,

$$PH_4I+KOH=PH_3+KI+H_2O$$

(Hofmann, Ber. 1871, 4, 200).

Very pure phosphine may readily and conveniently be prepared from a specially prepared mixture of calcium and aluminium phosphides by the action of water, the process being completed by the addition of hydrochloric acid. The only impurity in this case is a very small quantity of pure hydrogen (Matignon and Trannoy, Compt. rend. 1909, 148, 167).

Phosphine is a colourless gas with an offensive, garlic-like smell. Its density is 1·1829; it liquefies at −85°, solidifies at −133·5° (Olzewski) and has the critical temperature 52·8° and the critical pressure 64 atmospheres.

Phosphine may be mixed with oxygen without alteration, but if the pressure of the mixture be suddenly diminished, an explosion occurs. (Compare also Lemoult, Compt. rend. 1907, 145, 374). The gas also takes fire when brought into contact with dilute nitric acid or if mixed with the vapours of chlorine or bromine water and is decomposed into hydrogen and phosphorus by a series of electric sparks. Phosphine is a very poisonous gas, a small quantity, when breathed, producing in turn dyspnœa and death.

It is somewhat soluble in water and is absorbed by copper sulphate and mercuric chloride and bromide, forming the phosphides of the metals, and in some cases more complex salts (Joannis, Compt. rend. 1898, 127, 270; 1899, 128, 1322, 1398; 129, 336; Rubénovitch, *ibid.* 1898, 127, 270; 1899, 128, 1398; Ribeau, *ibid.* 128, 1452; Lemoult, *ibid.* 1907, 145, 1175).

Like ammonia, it also combines with metallic chlorides such as those of tin, antimony, aluminium, &c., and with hydrobromic and hydriodic acids to form phosphonium compounds, of which phosphonium iodide, PH_4I, is used as a powerful reducing agent and in the preparation of many organic phosphorus compounds.

Gattermann and Hausknecht (Ber. 1890, 1174) employ the following process for preparing the dihydride. A large three-necked Woulff's bottle, three-fourths filled with water, is freed from air by a current of hydrogen supplied through a tube fitted in one neck and dipping just beneath the water, and is heated in a water-bath to 60°. Calcium phosphide is then introduced in lumps weighing about 2 grams through a wide, funnel-topped tube fitted to the second neck and just dipping beneath the water. The evolved gases pass through a tube fitted to the third neck to a test-tube, from which passes a tube to a condensing-tube surrounded by iced water. The water in the gas condenses in the test-tube, and the hydride, P_2H_4, liquefies in the condenser, about 2 c.c. being obtained from 50 grams of calcium phosphide. The uncondensed gas may be passed through a flask containing hydrochloric acid, which decomposes the remaining P_2H_4 into the trihydride and the solid hydride.

The dihydride is a colourless liquid of sp.gr. 1·007 at 12°; boiling, when not too suddenly heated, at 57°–58° (735 mm.) (Gattermann and Hausknecht, *l.c.*). On exposure to light, or under the action of hydrochloric acid, it decomposes into the trihydride and the solid hydride. Small quantities of the dihydride impart spontaneous inflammability to hydrogen, carbon monoxide, and other combustible gases.

The solid hydride is obtained, as above, as a yellow powder, by decomposing the dihydride with hydrochloric acid, or by the action of light, or by treating calcium phosphide with hot hydrochloric acid, or by treating calcium phosphide with water and allowing the gas formed to come in contact with calcium chloride (Stock, Böttcher and Lenger, Ber. 1909, 42, 2839). It ignites when heated in the air.

After exposure to the air, it acquires an acid reaction and the odour of phosphine. It is quite stable in the dark, but in sunlight it becomes red and evolves an inflammable gas. In a vacuum it evolves pure phosphine, and this is recommended as a method of preparing the latter by Stock, Böttcher and Lenger (*l.c.*). The red substance which remains behind is, according to these authors, P_9H_2, produced thus, $5P_{12}H_6=6P_9H_2+6PH_3$. The hydride P_9H_2 is stable in dry air, but in moist air it decomposes forming phosphine and phosphoric acid. It dissolves in liquid ammonia forming a black compound varying in composition between P_9H_2,NH_3 and $2P_9H_2,NH_3$ (*ibid.* 2847).

Similar black compounds are produced by the union of the solid hydride $P_{12}H_6$ with ammonia and piperidine (Schenck, Ber. 1903, 36, 4202; Stock, *ibid.* 1903, 36, 1120; Stock, Böttcher and Lenger, *l.c.*).

Compounds of Phosphorus and Nitrogen.

A considerable number of these compounds exists.

Phosphorus nitride P_3N_5 can be obtained quantitatively and absolutely pure by saturating pure phosphorus pentasulphide with pure dry ammonia at the ordinary temperature, subsequently heating the products in an atmosphere of hydrogen, then in a current of ammonia at 850° (Stock and Hoffmann, Ber. 1903, 36, 314; Stock and Grüneberg, *ibid.* 1907, 40, 2573;

Stock and Johannsen, *ibid.* 1908, 41, 1593). It varies in colour from pure white to dark red, according to the time of heating in its preparation and has sp.gr. of 2·51 at 18°. At the ordinary temperature it is inactive, but acts as a powerful reducing agent at a high temperature. It is decomposed by many metals and by water at 180°. When heated in chlorine or oxygen it takes fire.

Phospham PN_2H(?) is obtained as an amorphous, light, white powder, insoluble in water and infusible at a red heat, when the product of the reaction of ammonia on phosphorus pentachloride is heated in the absence of air until fumes of ammonium chloride cease to be evolved (Besson, Compt. rend. 1892, 114, 1264; Besson and Rosset, *ibid.* 1908, 146, 1149). When dry, it is oxidised by heating in air, evolving white fumes; if previously moistened it decomposes thus:

$$3PHN_2+9H_2O=3HPO_3+6NH_3.$$

Phosphoramide $P(NH_2)_3$ is obtained by the action of ammonia on phosphorus tribromide or triiodide at −70° (Hugot, Compt. rend. 141, 1235). It is an unstable yellow solid which readily decomposes at 0°, forming phosphorimide, $P_2(NH)_3$, a brown solid which decomposes on heating into ammonia, nitrogen, and phosphorus (*v.* also Stock, Ber. 1903, 36, 1120).

Phosphamide (*phosphodiamide*) $PO(NH)NH_2$ is a white powder obtained by the action of water on the product of the action of ammonia on phosphorus pentachloride:

$$PCl_5+4NH_3=(NH_2)_2PCl_3+2NH_4Cl$$

and

$$(NH_2)_2PCl_3+H_2O=PO(NH)NH_2+3HCl.$$

Phosphoryl triamide (*phosphotriamide*) $PO(NH_2)_3$ is a white amorphous powder obtained by the action of dry ammonia on phosphorus oxychloride (Schiff, Zeitsch. öffentl. Chem. 5, 609).

Phosphorus diamide $POH(NH_2)_2$ is obtained by the action of ammonia on a solution of phosphorus oxide in ether or benzene. It is a white powder which dissolves in water with incandescence and is violently decomposed by dilute hydrochloric acid, forming phosphine, phosphoric and phosphorous acids, ammonium chloride and phosphorus (Thorpe and Tutton, Chem. Soc. Trans. 1891, 1027).

Phosphamidic acid or **amidophosphoric acid** $PO{\cdot}NH_2(OH)_2$, is formed by the action of dry ammonia on phosphorus pentoxide (Biltz, Ber. 1894, 27, 1257); or the potassium salt of the acid is obtained by the action of potassium hydroxide on the corresponding phenyl ester, the free acid being formed by the decomposition of the lead or silver salt by sulphuretted hydrogen and precipitating it from the filtrate with alcohol (Stokes, Amer. Chem. J. 1893, 15, 198; 16, 154). It forms colourless microscopic crystals having a sweet taste and forming both normal and acid salts.

Diamidophosphoric acid $PO(NH_2)_2OH$, is a crystalline compound obtained in the same way as the foregoing acid (Stokes, Ber. 1894, 27, 565). It forms the silver salts $(NH_2)_2PO{\cdot}OAg$ and $(NHAg)_2P(OAg)_3$.

A number of imido phosphoric acids have also been prepared (Stokes, Amer. Chem. J. 1896, 18, 629; 1898, 20, 740).

Phosphoryl nitride (*phosphomonamide*) PON is obtained when phosphamide is heated to redness out of contact with air. Several phosphamic acids, and amides containing chlorine, are also known (*v.* Gladstone, Chem. Soc. Trans. 1864, 225; 1865, 1; 1866, 1 and 290; Salzmann, Ber. 1874, 7, 494; Winter, J. Amer. Chem. Soc. 1904, 26, 1484; Stokes, Amer. Chem. J. 19, 782).

Compounds of phosphorus and sulphur.

Several liquid and solid sulphides, all of which are very inflammable and more fusible than either of the constituent elements, are known. The liquids SP_4 and SP_2 are not compounds but only solutions of sulphur in phosphorus (Boulouch, Compt. rend. 1902, 135, 165; Stock and Bezhold, Ber. 1908, 41, 657; Stock, *ibid.* 1909, 42, 2062). The solid sulphides, P_4S_3, P_3S_6, and P_2S_5 are obtained by carefully heating sulphur with amorphous phosphorus. The composition P_2S_6 (Dupré) or P_2S_{12} (Berzelius, Gmelin's Handb. 2, 218) has been assigned to a body obtained in rhombic sulphur-like crystals by solution of sulphur in sulphur diphosphide. According to Ramme (Ber. 1879, 12, 940, 1350), the crystals are merely sulphur containing phosphorus (*cf.* Boulouch, Compt. rend. 1906, 143, 41).

Phosphorus pentasulphide P_2S_5, which is employed in the preparation of organic sulphur compounds, is produced by gently heating a mixture of excess of powdered roll sulphur and amorphous phosphorus. A small portion of the mixture is first heated in a stream of carbon dioxide until reaction sets in. The source of heat is then removed and the rest of the mixture is added in small quantities. After cooling, the mass is extracted with boiling carbon disulphide (Stock and Scharfenberg, Ber. 1908, 41, 558). The product forms a greyish-yellow crystalline mass, which may be obtained in transparent crystals by sublimation. According to Stock and Thiel (Ber. 1905, 38, 2719), the pentasulphide exists in at least two modifications. The ordinary compound melts at 274°–276° (Meyer, *ibid.* 1879, 12, 610), and boils at 519° at 734 mm. pressure (Goldschmidt, *ibid.* 1882, 15, 304). The other modification melts at about 255°, is more soluble in carbon disulphide and can be obtained by the distillation of the ordinary sulphide *in vacuô* and rapidly cooling the product (Stock and Scharfenberg, *l.c.*).

Phosphorus pentasulphide dissolves in liquid ammonia forming ammonia thioiminophosphate compounds from which iminothiophosphoric acid has been obtained (Stock, Ber. 1906, 39, 1967).

Phosphorus sesquisulphide P_4S_3 forms rhombic prisms, m.p. 166°, b.p. 380°. It is easily inflammable and is slowly decomposed by boiling water forming sulphuretted hydrogen, phosphine, and phosphorous acid (Clayton, Chem. Soc. Proc. 1902, 129; *ibid.* 1903, 231; Mai and Scheffer, Ber. 1903, 36, 870). The commercial product sometimes contains free phosphorus, the presence of which can be detected by passing a current of hydrogen over the sulphide when, if phosphorus is present, the issuing gas will burn with a green flame.

In carbon disulphide solution, phosphorus sesquisulphide absorbs iodine forming $P_4S_3I_2$, orange-yellow crystals, m.p. 119·5°—this compound can be used as a means of detecting the sesquisulphide (Walter, Chem. Zeit. 1907, 31, 640). According to Gartenmeister (J. Soc. Chem. Ind. 1908, 837), easily inflammable but not explosive substances which are not sensitive to moisture can be obtained by heating together various proportions of red phosphorus, sulphur, and the sulphides of metals such as antimony, to about 170°.

Phosphorus sulphoxides $P_4O_6S_4$, m.p. 102°, b.p. 295°, and $P_2O_2S_3$, which decomposes at 200°, forming phosphorus pentoxide and pentasulphide, have been prepared by Thorpe and Tutton (Chem. Soc. Trans. 1891, 1024), and Besson (Compt. rend. 1897, 124, 151).

For other work on phosphorus sulphides, *v.* Rebs (Annalen, 1888, 246, 356), Dervin (Bull. Soc. chim. 41, 433), Isambert (Compt. rend. 1883, 96, 1499, 1771), Lemoine (*ibid.* 1630), Schulze (Ber. 1883, 16, 2066), Frouin (Chem. Zeit. Rep. 1899, 23, 213), Weelwright (J. Soc. Chem. Ind. 1903, 229), Boulouch (Compt. rend. 1904, 138, 363; 1906, 142, 1045; 143, 41), Dervin (*ibid.* 138, 366), Girvan (*ibid.* 142, 398), Stock (Ber. 1909, 42, 2062).

Compounds of phosphorus and selenium.

Phosphorus and selenium can be fused together in all proportions, a red mass being formed; the only definite compounds, however, are P_4Se_3, P_2Se_5, and possibly P_2Se_3. These compounds are decomposed by moist air, and when treated with alkalis or alkali sulphides yield complex salts such as potassium thioselenophosphite $2K_2S,P_2Se_3,5H_2O$ (*v.* Berzelius, Gmelin's Handb. 2, 242; Bogen, Annalen, 1862, 124, 57; Hahn, J. pr. Chem. [i.] 93, 430; Muthmann and Clever, Zeitsch. anorg. Chem. 1896, 13, 191; Meyer, *ibid.* 1902, 30, 258).

Haloid compounds of phosphorus.

Phosphorus trichloride PCl_3, may be prepared by passing dry chlorine over heated amorphous phosphorus or over dry ordinary phosphorus, and digesting the product with ordinary phosphorus for some weeks to convert any pentachloride which may have been formed into the trichloride (Dumas, Ann. Chim. Phys. [iii.] 55, 172). It is a mobile, colourless, fuming liquid of pungent smell, boiling at 75·95° (760 mm.), and having a sp.gr. of 1·61275 $\frac{0°}{4°}$ (Thorpe, Proc. Roy. Soc. 24, 295). It absorbs water with production of hydrochloric and phosphorous acids and a small quantity of phosphorus oxychloride, $POCl_3$ (Besson, Compt. rend. 1898, 125, 771). It dissolves phosphorus, and is itself soluble in benzene and carbon disulphide. When mixed with alcohol, heat is evolved, with production of ethyl chloride and phosphorous acid, and evolution of hydrochloric acid. Phosphorous ester is also produced (Béchamp. Compt. rend. 1855, 40, 944; 41, 23). It also unites with ammonia forming additive compounds (Besson, *ibid.* 1890, 111, 972).

Phosphorus trichloride reacts with glycerol and with glycol, yielding in the former case phosphorous esters of glycerol and of monochlorhydrin which are decomposed by water forming the compounds $P_2(OH)_4O_2{\cdot}C_3H_5OH$ and $P(OH)_2O{\cdot}C_3H_5OHCl$ of which the calcium derivatives have been isolated (Carré, Compt. rend. 1903, 136, 1456).

Phosphorus pentachloride PCl_5 may be obtained by passing dry chlorine over the well-cooled trichloride until the whole is dry, or by the action of excess of chlorine on phosphorus. On the large scale, it is best prepared by passing excess of dry chlorine through a cooled solution of phosphorus in carbon disulphide, and finally crystallising out the product. It forms white lustrous crystals of unpleasant smell, volatilising below 100° without liquefying. Under pressure, it melts at 148° (Strecker). The vapour decomposes, when heated, into the trichloride and chlorine (Wanklyn and Robinson, Proc. Roy. Soc. 12, 507; Wegscheider, Monatsh. 1899, 20, 307).

In moist air, the pentachloride is converted into the oxychloride with evolution of hydrochloric acid. Sulphur trioxide converts it into the oxychloride with production of sulphuryl chloride: $SO_3+PCl_5=SO_2Cl_2+POCl_3$. Phosphorus pentachloride is much used in the preparation of organic chlorides. It forms chloramino derivatives or an additive compound with ammonia, depending on the temperature of the reaction (Besson, Compt. rend, *l.c.*).

Both chlorides form additive compounds with certain chlorides and bromides such as $PCl_3,2BBr_3$; $PCl_5,2BBr_3$, &c. (Tarible, Compt. rend. 1901, 132, 83; Strecker and Schurigin, Ber. 1909, 42, 1767).

Phosphorus chlorobromide PCl_3Br_2 is obtained by the action of bromine on phosphorus trichloride. It solidifies at −20°, and decomposes when heated to 35° (Michaelis, Ber. 1872, 5, 9). It combines with various proportions of bromine (*v.* Michaelis, *l.c.*; Prinvault, Compt. rend. 1872, 74, 868; and Stern, Chem. Soc. Trans. 1886, 815).

Phosphorus chloro-iodide PCl_3I_2 is said to be obtained in fine red hexagonal crystals by the action of iodine on phosphorus trichloride (Moot, Ber. 1879, 13, 2029).

Phosphoryl chloride (phosphorus oxychloride) $POCl_3$ may be prepared by heating dry oxalic or boric acid with the pentachloride:

$$PCl_5+H_2C_2O_4=POCl_3+2HCl+CO_2+CO,$$

or by heating the pentachloride with the pentoxide in a sealed tube: $3PCl_5+P_2O_5=5POCl_3$. It can be conveniently prepared by the action of potassium chlorate on phosphorus trichloride (Dervin, Compt. rend. 1883, 97, 576; Ullmann and Fornaro, Ber. 1901, 34, 2172); or, according to Erdmann (Zeitsch. angew. Chem. 1903, 89), by passing a current of dry chlorine over a strongly heated, powdered mixture of carbon and a metaphosphate.

Phosphoryl chloride is a colourless, fuming liquid, boiling at 107·23° (760 mm.), and having a sp.gr. of 1·71163 $\frac{0°}{4°}$ (Thorpe, Chem. Soc. Trans. 37, 338). When cooled it solidifies to crystals which melt at −1·5° (Geuther and Michaelis, Ber. 1871, 4, 769). Its molecular depression of the freezing-point is 0·48° (Huntley, Chem. Soc. Trans. 1891, 205). Water rapidly decomposes it into hydrochloric and phosphoric acids. It forms crystalline double compounds with many metallic chlorides.

Metaphosphoryl chloride (?) PO_2Cl. A straw-coloured viscous body obtained, together with phosphoryl chloride, by the action of chlorine on cooled phosphorous oxide (Thorpe and Tutton, Chem. Soc. Trans. 1890, 572); has been found to possess a composition corresponding with the formula PO_2Cl. It has, however, been shown by Huntley (*ibid.* 1891, 202) that this body consists of at least two substances, one of which is pyrophosphoryl chloride, whilst the other is a compound or mixture of the composition $P_7O_{15}Cl_5$.

According to Besson (Compt. rend. 1897, 124, 1099), metaphosphoryl chloride is obtained by the action of a small amount of water on phosphoryl chloride.

Pyrophosphoryl chloride $P_2O_3Cl_4$ is a colourless, fuming liquid, boiling between 210°–215°. It is obtained by the action of nitrogen peroxide on cooled phosphorus trichloride. Nitrosyl chloride is evolved, and pyrophosphoryl chloride remains, together with phosphorus pentoxide, phosphorus trichloride, and phosphoryl chloride, from which it is separated by fractional distillation (Geuther and Michaelis, Ber. 1871, 4, 767). It is also obtained as stated above or by the action of water on phosphorus pentachloride or by treating the pentachloride (6 parts) with the pentoxide (1 part) (Oddo, Gazz. chim. ital. 1899, [ii.]29, 330).

Phosphoryl bromodichloride $POBrCl_2$ (*v.* Menschutkin, J. pr. Chem. [i.] 98, 485; Besson, Compt. rend. 1896, 122, 814), is a highly refractive liquid, boiling at 135°–138° (760 mm.), and having a sp.gr. of 2·12065 $\frac{0^\circ}{4^\circ}$ (Thorpe, Chem. Soc. Trans. 37, 344). When cooled, it solidifies in tables, which melt at 11° (Geuther and Michaelis, Ber. 1871, 4, 769; 13° (Besson, *l.c.*).

By the action of hydrogen bromide on phosphoryl chloride at 400°–500°, it is obtained together with *phosphoryl dibromochloride* $POBr_2Cl$, which melts at 30° and has b.p. 165° (Besson, *l.c.*).

Thiophosphoryl chloride $PSCl_3$, is a colourless, fuming liquid, produced by the action of sulphuretted hydrogen on the pentachloride, or, better, by heating a mixture of phosphorus pentasulphide and pentachloride. It boils at 125° (760 mm.), and has a sp.gr. of 1·6682 $\frac{0^\circ}{4^\circ}$ (Thorpe, Chem. Soc. Trans. 37, 341).

Nitrogen chlorophosphide $PNCl_2$ is obtained by gently heating a mixture of phosphorus pentachloride and mercurammonium chloride (white precipitate) or ammonium chloride (Stokes, Ber. 1895, 28, 437; Amer. Chem. J. 1896, 18, 629, 780; *ibid.* 1897, 19, 782; *ibid.* 1898, 20, 740; Besson, Compt. rend. 1892, 114, 1264, 1479; Besson and Rossett, *ibid.* 1906, 143, 37). It sublimes in rhombic prisms, melting at 110°, and boiling at 240° (*v.* Gladstone and Holmes, Chem. Soc. Trans. 17, 225).

With liquid ammonia, nitrogen chlorophosphide reacts thus:

$$PNCl_2+4NH_3=2NH_4Cl+PN(NH_2)_2.$$

The compound PN_3H_4 is a white substance soluble in water, and on heating to 222° loses ammonia and is converted into phospham. Nitrogen chlorophosphide in carbon tetrachloride solution, when treated with dry ammonia gas, yields slender silky needles of the compound, $P_2N_3H_2Cl_3$, together with some PN_3H_4 (Besson, Compt. rend. 1908, 146, 1149).

A number of nitrogen chlorophosphides, all corresponding with the empirical formula $(PNCl_2)_x$ have been obtained.

Phosphorus tribromide PBr_3 is best prepared by slowly dropping bromine on to excess of amorphous phosphorus in a flask fitted with an inverted condenser, or by dropping bromine on to ordinary phosphorus covered by a layer of benzene (Christomanos, Ber. 1904, 37, 2883). The rectified product is a colourless mobile liquid of strong, pungent smell, boiling at 172·9° (760 mm.), 170·8° (Christomanos), solidifying at −41·5°, and having a sp.gr. of 2·923 $\frac{0^\circ}{4^\circ}$ (Thorpe, Chem. Soc. Trans. 37, 335). It acts as a reducing agent on many organic compounds, and forms double salts of the type $CuBr_3,PBr_3$ (Arbusoff, J. Russ. Phys. Chem. Soc. 1906, 38, 293).

Phosphorus pentabromide PBr_5 is produced by the addition of bromine to the cooled tribromide; it forms yellow crystals of pungent smell, melting to a red liquid, which decomposes into the tribromide and bromine at 100°. According to Castle and Beaty (Amer. Chem. J. 1899, 21, 322; *ibid.* 1900, 23, 505), when the pentabromide is mixed with bromine and sublimed, red prisms of a *heptabromide*, PBr_7, are formed.

Phosphorus trifluorodibromide PF_3Br_2 has also been obtained.

Phosphoryl bromide (phosphorus oxybromide) $POBr_3$ occurs in flat tables, melting at 45°–46° and boiling at 195° (Ritter, J. 8, 301), and is prepared similarly to phosphoryl chloride.

According to Berger (Compt. rend. 1908, 146, 400), it forms colourless crystals, m.p. 55°–56°, b.p. 189·5° (774 mm.).

Phosphonium bromide PH_4Br crystallises in colourless cubes, b.p. 30° and resembles the iodine compound.

Thiophosphoryl bromide $PSBr_3$, a yellow, crystalline body, m.p. 38°, *pyrothiophosphoryl bromide* $P_2S_3Br_4$, a fuming yellow oily liquid, and *metathiophosphoryl bromide* PS_2Br, are also known.

Bromo-chloro-thio compounds of phosphorus have been prepared by Besson (Compt. rend. 1896, 122, 1057).

Phosphorus di-iodide P_2I_4 is prepared by the gradual addition of 8·2 parts of iodine to a solution of 1 part of phosphorus in carbon disulphide. On distilling off the disulphide, or on cooling it, the iodide remains or crystallises out in bright orange-yellow crystals which fuse at about 110° (Corenwinder, Ann. Chim. Phys. [iii.] 30, 242).

A rapid and safe method of producing phosphorus di-iodide is described by Doughty (J. Amer. Chem. Soc. 1905, 27, 1444); 50 grams of iodine and 4 grams of red phosphorus are heated in a 200 c.c. flask over a free flame until melted. After cooling to 60°, 2·5 grams of yellow phosphorus are added in small pieces.

When dry iodine is added to a solution of phosphorus in dry carbon disulphide, in quantity less than that necessary to convert the phosphorus into the di-iodide and the mixture is exposed to sunlight, *phosphorus subiodide*, P_4I, separates.

It is an amorphous, red powder which decomposes without melting and is decomposed by most reagents (Boulough, Compt. rend. 1905, 141, 256).

Phosphorus tri-iodide PI_3 is prepared similarly to the di-iodide, but with the use of a correspondingly larger proportion of iodine. It forms red six-sided deliquescent prisms, m.p. 61° (Corenwinder, *l.c.*, Snape, Chem. News, 1896, 74, 27; Besson, Compt. rend. 1897, 124, 1346).

Phosphonium iodide PH_4I is obtained by the union of phosphine with hydriodic acid, or by the action of water and iodine on excess of phosphorus.

The iodine and phosphorus are preferably combined in carbon disulphide, which is then distilled off and the water added gradually during passage of carbon dioxide (Hofmann, Ber. 1873, 6, 291). The iodide is thus obtained as a sublimate of glistening deliquescent quadratic prisms, b.p. about 80° but readily vapourising at a lower temperature, decomposed by water into hydriodic acid and phosphine. It is a powerful reducing agent, and is employed as such in the preparation of many organic compounds.

Phosphorus thioiodide, P_2SI_2, m.p. 75° (Besson, Compt. rend. 1896, 122, 1057), and P_2S_3I (Ouvrard, *ibid.* 1892, 115, 1301) also exist.

Phosphorus trifluoride PF_3 may be prepared by carefully heating dry copper phosphide with lead fluoride, or by allowing arsenic trifluoride to drop upon phosphorus trichloride, or, preferably, by gently warming a mixture of dry zinc fluoride and phosphorus tribromide. It is a colourless sharp-smelling gas, which condenses at −10° under a pressure of 40 atmospheres to a colourless mobile liquid, b.p. −95°, and solidifying at −160°. The gas dissolves slowly in water. It produces silicon fluoride, with separation of phosphorus, when heated in contact with glass. It combines directly with bromine, giving an amber-coloured mobile liquid having the composition PF_3Br_2 (Moissan, Compt. rend. 1884, 99, 655, 970; 1885, 100, 272, 1348; Ann. Chim. Phys. [vi.] 19, 286).

Phosphorus pentafluoride PF_5 is obtained by the action of arsenic trifluoride on phosphorus pentachloride (Thorpe, Proc. Roy. Soc. 1876, 122). It is a heavy, fuming, colourless, uninflammable gas, which is rapidly decomposed by water into hydrofluoric acid and phosphoric acid. It combines with dry ammonia to produce a white solid $2PF_5{\cdot}5NH_3$, and, according to Tassel (Compt. rend. 1890, 110, 1264), combines with nitrogen peroxide to produce a white crystalline compound of the composition $PF_5{\cdot}NO_2$; *v.* also Moissan (*ibid.* 1885, 101, 1490; 1886, 103, 1257). It condenses to a liquid, b.p. −75° and solidifies to a flocculent mass at −83° (Moissan, *ibid.* 1904, 138, 789).

Phosphoryl fluoride, phosphorus oxyfluoride POF_3 may be prepared by the action of the electric spark on a mixture of phosphorus trifluoride and oxygen, by the action of phosphorus oxychloride on gently warmed zinc fluoride (Moissan, Compt. rend. 1886, 102, 1245; Bull. Soc. chim. 1891, [iii.] 5, 458), or, better, by the method employed by Thorpe and Hambly (Chem. Soc. Trans. 1889, 759), which consists in gently heating a mixture of cryolite and phosphorus pentoxide. It is a colourless, fuming gas, rapidly absorbed by water, and without action, when dry, on glass or mercury. It condenses to a liquid which boils at −40° and solidifies to a crystalline mass at −68° (Moissan, *l.c.*).

Thiophosphoryl fluoride PSF_3 may be obtained by heating a mixture of arsenic trifluoride and phosphorus thiochloride in a sealed glass tube to 150°, or by heating a mixture of amorphous phosphorus, sulphur, and lead or bismuth fluoride, or, preferably, by heating a mixture of powdered, freshly-fused lead fluoride, and freshly-made phosphorus pentasulphide in a leaden tube from which air has been expelled by a current of dry nitrogen: $P_2S_5+3PbF_2=3PbS+2PSF_3$. The action commences at 170°, and the temperature should be kept below 250°. The gas is stored over mercury in a glass holder containing fragments of quicklime, which gradually absorb the phosphorus trifluoride and any trace of silicon fluoride contained in the gas. The quicklime should be freed from air before use by repeatedly passing dry nitrogen into the holder and exhausting with a Sprengel pump. At ordinary temperatures, thiophosphoryl fluoride is a heavy colourless gas which condenses at a pressure of 10 to 11 atmospheres to a colourless liquid. A jet of the gas burns spontaneously with a greyish-green flame of extremely low heating power. If a considerable quantity of the gas be suddenly exposed to the air, a fine blue flash, followed by the greyish-green flame, is observed. The gas burns spontaneously with a yellow flame in oxygen, but the dry gas does not inflame in dry oxygen in presence of sufficient of its oxidation products. The mixture instantly inflames on exposure to air or on introduction of moisture.

When heated or exposed to the electric spark, the gas is decomposed into sulphur, phosphorus, and phosphorus fluorides. It is without action on mercury, sulphuric acid, carbon disulphide, or benzene. It dissolves to some extent in ether, the solution burning with a greenish flame. It dissolves slowly with decomposition in water and solution of potash, soda, or ammonia. It combines with ammonia gas to form a white solid. Gently heated sodium burns with a red flame in the gas, the residue evolving spontaneously inflammable phosphine when treated with water. When heated in a glass tube the gas deposits phosphorus and sulphur, with formation of silicon tetrafluoride, which occupies three-fourths of the volume of the original gas: $4PSF_3+3Si=3SiF_4+P_4+S_4$ (Thorpe and Rodger, Chem. Soc. Trans. 1888, 766; 1889, 306).

Oxides and acids of phosphorus.

The product of the combustion of phosphorus in a limited supply of air consists of a mixture of the four oxides P_4O, P_4O_6, P_2O_4, and P_4O_{10}.

The first of these oxides, P_4O, was obtained by Le Verrier (Annalen, 1838, 27, 167), but whilst its existence has been maintained by some chemists, this is denied by many others (Michaelis and Pitsch, *ibid.* 1899, 310, 45; Michaelis and Arend, *ibid.* 1900, 314, 259; 1902, 325, 361; Biltz, Ber. 1894, 27, 1257; Besson, Compt. rend. 1897, 124, 763; 1897, 125, 1032; 1901, 132, 1556; Chapman and Libury, Chem. Soc. Trans. 1899, 973; Burgess and Chapman, *ibid.* 1901, 1235; Browning, Chem. Soc. Proc.

1901, 243; Jungfleisch, Compt. rend. 1907, 145, 325).

Phosphorous oxide, phosphorous anhydride P_4O_6. The existence of this compound as one of the products of the slow combustion of phosphorus seems to have been first noticed by Sage in 1777. It appears also to have been obtained by Cabell as a sublimate from the mixed oxides (Chem. News, 50, 209). It, however, received no systematic examination until Thorpe and Tutton (Chem. Soc. Trans. 1890, 545; 1891, 1019) obtained it in a state of purity by the following method:—

Pieces of dried phosphorus are placed in a glass tube drawn out, but open at one end, and connected at the other end with a brass tube surrounded by a tube filled with water. The inner tube is connected with a long-limbed U-tube fitted at the bend with a branch leading to a small bottle, into which the product of the action may be passed by warming the limbs of the U-tube. A freezing mixture surrounds the U-tube and bottle.

The phosphorus having been ignited by heating the tube, is oxidised by drawing air through the apparatus with an aspirator, and after about 15 minutes, the water around the brass tube is heated to about 50°, as indicated by a thermometer fitted to the outer tube, and the temperature is maintained thereabouts until near the end of the operation, when it is raised to about 60°. The readily fusible trioxide gradually passes over from the combustion products in the brass tube and solidifies in the U-tube, a loose plug of glass wool in the brass tube preventing passage of the other oxides. The action is stopped when about four-fifths of the phosphorus has been burned, in order to diminish the chance of oxidising the product.

The product solidifies in the U-tube as a snow-white waxy mass. It may also be obtained in long feathery aggregations or in thin isolated prisms, terminated by pyramids, and probably belonging to the monoclinic system, as do those of the corresponding compound with arsenic or antimony.

According to Jungfleisch (*l.c.*), a continuous yield of well-defined crystals of phosphorous oxide can be obtained by oxidising pure dry phosphorus at a low temperature at 18–20 mm. pressure.

Phosphorous oxide possesses a peculiar phosphorus-like smell. It fuses at 22·5° to a mobile liquid, sp.gr. 1·9358 $\frac{24{\cdot}8^\circ}{4^\circ}$, which normally re-solidifies at 21°, but which sometimes exhibits the property of superfusion. It boils at 173·1° (760 mm.). When heated in a sealed tube to about 210° the oxide becomes turbid, and at 440° is entirely decomposed into the tetroxide and amorphous phosphorus.

Phosphorous oxide is slowly dissolved by cold water, forming phosphorous acid. With hot water the action is violent, large quantities of the red suboxide or amorphous phosphorus being produced, with evolution of spontaneously inflammable phosphine.

Phosphorous oxide dissolves unchanged in ether, carbon disulphide, benzene, or chloroform, but is instantly ignited in contact with absolute alcohol. When this action is properly controlled, *di-ethyl phosphorous acid* is obtained.

The oxide is spontaneously oxidised in presence of air or oxygen. When thrown into oxygen heated at 50° or 60°, it ignites with great brilliancy. It inflames readily when exposed to the air, especially when warmed or when in contact with fabrics or paper. When thrown into chlorine, it burns with a greenish flame. The slow action of chlorine on the cooled oxide gives a mixture of phosphoryl chloride and the so-called metaphosphoryl chloride.

Bromine acts in a similar manner, but with previous formation of phosphorus pentabromide. With iodine it forms the tetraiodide and the pentoxide: $5P_4O_6+8I_2=4P_2I_4+6P_2O_5$. Heated with sulphur it yields phosphorus sulphoxide $P_4O_6S_4$, forming clear transparent crystals, m.p. 102° and b.p. 295°, deliquescing rapidly in the air, and readily dissolved by water, forming sulphuretted hydrogen and phosphoric acid: $P_4O_6S_4+10H_2O=4H_3PO_4+4H_2S$ (Thorpe and Tutton, Chem. Soc. Trans. 1891, 1023).

Vapour density determinations show that the gaseous molecule of the oxide has the formula P_4O_6. Determinations of the molecular weight by Raoult's method give similar results.

Phosphorus tetroxide P_2O_4 was first obtained by Thorpe and Tutton (Chem. Soc. Trans. 1886, 833) by heating the mixed oxides obtained by the slow combustion of phosphorus in a sealed exhausted tube at about 290°. A sublimate of this oxide in clear, transparent, lustrous, colourless, orthorhombic crystals, volatilising at about 180°, is thus obtained. It may be prepared, together with amorphous phosphorus, by heating phosphorous oxide in a sealed tube to about 440°.

This oxide is highly deliquescent and dissolves in water, with evolution of heat, the strongly acid solution being unchanged on boiling. The solution reduces mercuric chloride to calomel on warming, and gives a white precipitate, which rapidly blackens with silver nitrate. Its vapour density at 1400° is 230 (West, Chem. Soc. Trans. 1902, 933).

Phosphorus pentoxide, phosphoric oxide, phosphoric anhydride P_4O_{10} is the product of the complete combustion of phosphorus. It may be obtained in a state of purity by suspending a porcelain dish, containing burning phosphorus, in a three-necked globe, and drawing dried air through the globe with an aspirator. Two of the necks serve for the entrance and exit of the air, and the third and vertical neck receives a corked tube, through which pieces of dried phosphorus are dropped at intervals into the dish.

Grabowski (Annalen, 1865, 136, 119) recommends for the preparation on the large scale the use of a sheet-iron cylinder, having a cover and resting on a sheet-iron funnel. The cover has a chimney closed by a cork, and a damper is fitted to the apparatus so that the air may be admitted as required. The oxide produced is shaken at intervals into a bottle beneath the funnel.

This oxide is a white amorphous powder which, when pure, is perfectly colourless and odourless. It frequently possesses a garlic smell, from the presence of phosphorous oxide, and may have a yellowish colour, more noticeable when a portion is allowed to deliquesce, from presence of the lower oxide P_4O or of red phosphorus. To free the oxide from all traces of lower oxides, it should be distilled over platinum sponge in a current of oxygen, until the product no longer reduces silver nitrate solution (Threlfall, Phil. Mag. 1893 [v.] 35, 14; Shenstone and Beck, Chem. Soc. Trans. 1893, 473). It rapidly deliquesces, with production of metaphosphoric acid. When added to water, orthophosphoric acid is gradually produced, with evolution of heat. According to Hautefeuille and Perrey (Compt. rend. 1884, 99, 33), it exists in three forms, crystalline, pulverulent and vitreous (Giran, *ibid.* 1903, 136, 550).

Phosphorus pentoxide is the best desiccating agent known, and is largely used in the laboratory for completing the desiccation of gases and liquids, or for removing the elements of water from compounds, as in the preparation of nitrogen pentoxide. Phosphorus pentoxide, when completely pure is capable of becoming highly phosphorescent *in vacuô* (Ebert and Hoffmann, Zeitsch. physikal. Chem. 1900, 80).

According to Besson (Compt. rend. 1897, 124, 763), the oxide P_2O also exists.

Hypophosphorous acid H_3PO_2 is a monobasic acid the salts of which are formed when alkalis or alkaline earths are boiled with phosphorus. The barium salt $Ba(PH_2O_2)_2$ is of most interest, as the acid and salts are usually prepared from it. This salt is formed, with evolution of phosphoretted hydrogen, on boiling phosphorus with baryta water:—$3Ba(OH)_2+2P_4+6H_2O =3Ba(PH_2O_2)_2+2PH_3$. It may be decomposed by dilute sulphuric acid to obtain the acid, or by the addition of a sulphate to produce another hypophosphite (Marie, Compt. rend. 1904, 138, 1216).

Hypophosphorous acid forms a thick syrup, from which crystals melting at 26·5° (Marie) may be obtained by evaporation below the boiling-point of the solution, and cooling in a freezing mixture. When strongly heated, it decomposes into phosphoretted hydrogen and phosphoric acid. It reduces mercuric chloride to calomel or mercury (Sieverts, Zeitsch. anorg. Chem. 1909, 64, 29), and is oxidised to phosphoric acid by chlorine and other oxidising agents (Steele, Chem. Soc. Proc. 1908, 193). When concentrated it attacks glass and porcelain more readily than phosphoric acid. Most hypophosphites dissolve in water, and many in alcohol. They are all powerful reducing agents, and precipitate gold and silver from solution. The sodium salt is used in medicine. For the preparation of hypophosphites, compare Kendal (J. Soc. Chem. Ind. 1890, 1129).

According to Mai (Ber. 1902, 35, 162), hypophosphorous acid reacts with organic diazo compounds forming hydrocarbons, this being in some cases an advantageous method of forming the latter. When boiled with acetone, hypophosphorous acid yields crystalline products, $H_3PO_2{\cdot}2C_3H_6O$; $H_3PO_2{\cdot}C_3H_6O$; and $H_3PO_3{\cdot}C_3H_6O$ (Marie, Compt. rend. 1901, 133, 219).

Phosphorous acid $P(OH)_3$ is obtained by the action of water on phosphorous oxide or of moist air on phosphorus. The pure acid may be obtained by the decomposition of phosphorus trichloride with water, or by slowly passing chlorine through a deep layer of phosphorus melted under water—

$$PCl_3+3H_2O=P(OH)_3+3HCl.$$

On evaporating the solution until it attains a temperature of 180° and forms a thick syrup, it gives on cooling a crystalline mass melting at 70·1° (Thomsen, Ber. 1874, 7, 996). When strongly heated, the acid produces phosphoretted hydrogen and phosphoric acid. The aqueous solution slowly absorbs oxygen. It is a powerful reducing agent, and precipitates gold, silver, and mercury from solution.

Phosphorous acid is tribasic, but, excepting the tribasic sodium salt and some ethereal salts, only two atoms of hydrogen are replaceable by the base. All phosphites are soluble in water, the normal alkaline salts being most soluble. They act as reducing agents similarly to the hypophosphites, but, unlike them, give a precipitate with lime water.

Pyrophosphorous acid $H_4P_2O_5$ is obtained by passing the vapour of phosphorus trichloride volatilised by a stream of carbon dioxide through the product of the reaction of water on an excess of the trichloride for 20 hours. It is then placed in a vacuum over fused potash and phosphorus pentoxide. It can also be obtained by the continuous agitation for about 5 hours at 30°–40° of a mixture of phosphorous acid and phosphorus trichloride. It melts at 38°, is readily decomposed by water, at 130° gives off phosphine and at 45° in presence of phosphorus trichloride yields phosphorus and phosphoric or pyrophosphoric acid (Auger, Compt. rend. 1903, 136, 814). The pyrophosphites, such as $Na_4P_2O_5$ also exist.

Phosphoric acids. Three acids, produced by the combination of phosphorus pentoxide with one, two, and three molecules of water respectively, are known, their names and composition being as follows: *Metaphosphoric acid* HPO_3 or $P_2O_5H_2O$; *pyrophosphoric acid* $H_4P_2O_7$ or $P_2O_52H_2O$; and *orthophosphoric acid* H_3PO_4 or $P_2O_53H_2O$. The sodium and silver salts of a fourth acid $P_4O_7(HO)_6$ or $2P_2O_5{\cdot}3H_2O$, which may be called tetraphosphoric acid, are also known (Fleitmann and Henneberg, Annalen, 1848, 65, 324). Salzer (*ibid.* 1877, 187, 322) has described a phosphoroso-phosphoric acid or hypophosphoric acid $P_4O_4(HO)_8$ of which phosphorus tetroxide may perhaps be the anhydride (Rosenheim and Pritze, Ber. 1908, 41, 2708). Finally, the sodium salt of *thiophosphoric acid* H_3PSO_3 (Wurtz, Ann. Chim. Phys. [iii.] 20, 472), and the salts of di- and tri- thiophosphoric acid, $H_3PS_2O_2$ and H_3PS_3O are also known (Kubierschky, J. pr. Chem. 1885, [ii.] 31, 93).

Several series of thiophosphates have been prepared by heating the metals with phosphorus and sulphur (Ferrand, Bull. Soc. chim. 1895, [iii.] 13, 115; Compt. rend. 1896, 122, 886).

Orthophosphoric acid H_3PO_4, usually known as 'phosphoric acid,' is a tribasic acid which is produced when amorphous phosphorus is heated with concentrated nitric acid (Watson, J. Soc. Chem. Ind. 1892, 224). The phosphorus slowly dissolves, with evolution of red fumes, and the solution is evaporated in a dish with repeated additions of nitric acid until red fumes cease to be evolved, to ensure the absence of phosphorous acid.

The acid is prepared commercially from bone-ash by digesting 3 parts of the ash with 3 parts of crude sulphuric acid (1·55) and 18 or 20 parts of water for two or three days. The solution, which contains the phosphorus as calcium tetrahydric diphosphate ('superphosphate of lime'), is then pressed in linen filters from the precipitated calcium sulphate, and is concentrated to a syrup, treated with concentrated sulphuric acid to precipitate the lime, and the solution filtered off, evaporated, and heated to remove the sulphuric acid. By another process the solution is treated with ammonium carbonate, which precipitates the lime and leaves triammonium phosphate in solution. The solution is separated and evaporated, and ignited to expel the ammonia. The acid obtained by either method contains magnesia and other impurities.

In another process the bone ash is dissolved in its own weight of hydrochloric acid of sp.gr. 1·18, diluted with 4 parts of water and 1½ parts of sodium sulphate is added. The filtered solution is neutralised while hot with sodium carbonate, refiltered, and precipitated with barium chloride. The mixture of barium sulphate and phosphate thus obtained is decomposed by sulphuric acid.

The bones, apatite or horn piths, &c., may be dried, ground, and digested with aqueous phosphoric acid, after which the product is treated with sulphuric acid (Lomas, J. Soc. Chem. Ind. 1900, 836; Eng. Pat. 9611).

According to Maywald (J. Soc. Chem. Ind. 1908, 1151), phosphoric acid may be manufactured by maintaining a low potential arc produced by a current of 60 volts, in a granular mass of phosphates to which air has access: the phosphoric acid is volatilised and collected.

Other manufacturing methods are described by Hatmaker (J. Soc. Chem. Ind. 1902, 1533; Powter, *ibid.* 1904, 252; Bandon, *ibid.* 1904, 787).

Commercial phosphoric acid frequently contains arsenic, either from the phosphorus used or from the acid employed in dissolving the bones, &c. The arsenic may be removed by reducing it to arsenious oxide with sulphurous acid, and precipitating it by passage of sulphuretted hydrogen, after removing the excess of the sulphurous acid by boiling.

To avoid the necessity for removing the arsenic, Wenzell (Proc. Am. Pharm. Assoc. 1882, 556, and Pharm. J. [iii.] 14, 24) prepared the acid by the slow, spontaneous oxidation of phosphorus in trays containing a thin layer of water. The phosphorous acid thus produced contains the arsenic as arsenious oxide, which becomes reduced to the elemental state, so that it may be separated by filtration, when the solution is heated to about 190° for half an hour. The filtered solution is oxidised to phosphoric acid by the action of nitric acid (Runyon, Pharm. J. [iii.] 14, 48; Sommer, J. Soc. Chem. Ind. 1885, 574).

To prepare the pure acid the commercial acid may be precipitated as the lead salt by addition of lead acetate, the precipitate being washed and decomposed by subjecting it while suspended in water to the action of sulphuretted hydrogen, or by treating it with dilute sulphuric acid. In the latter case the solution must be evaporated and heated to remove sulphuric acid, and be then redissolved and freed from traces of lead by means of sulphuretted hydrogen.

Phosphoric acid for medicinal purposes is also prepared by dissolving the pentoxide in water.

According to Nicolas (Compt. rend. 1890, 111, 974), pure phosphoric acid may be prepared by gradually adding pure calcium phosphate to a slight excess of pure dilute hydrofluoric acid contained in a lead or platinum vessel, the mixture being well stirred after each addition. The high temperature of the mixture is maintained for some time to complete the reaction; the calcium fluoride formed is removed by filtration and the filtrate, consisting of a solution of phosphoric acid, is evaporated until a thick syrup is obtained. By further evaporation, meta- and pyrophosphoric acids can be obtained.

By evaporation of its solution *in vacuô* over sulphuric acid, orthophosphoric acid may be obtained in hard, transparent, deliquescent, six-sided ortho-rhombic prisms fusing at 38·6° and losing water at 160°. At about 215° the acid is converted into pyrophosphoric acid, and when heated until dense white fumes begin to be evolved is converted into a highly deliquescent glassy mass of metaphosphoric acid.

The strength of aqueous solutions at 15·5° is shown in the following table (J. Watts, Chem. News, 1865, 12, 160):—

Specific gravity	P_2O_5 in 100 parts	Specific gravity	P_2O_5 in 100 parts
1·508	49·60	1·247	28·24
1·492	48·41	1·236	27·30
1·476	47·10	1·226	26·30
1·464	45·63	1·211	24·79
1·453	45·38	1·197	23·23
1·442	44·13	1·185	22·07
1·434	43·95	1·173	20·91
1·426	43·28	1·162	19·73
1·418	42·61	1·153	18·81
1·401	41·60	1·144	17·89
1·392	40·86	1·136	16·95
1·384	40·12	1·124	15·64
1·376	39·66	1·113	14·33
1·369	39·21	1·109	13·25
1·356	38·00	1·095	12·18
1·349	37·37	1·081	10·44
1·339	36·74	1·073	9·53
1·328	36·15	1·066	8·62
1·315	34·82	1·056	7·39
1·302	33·49	1·047	6·17
1·293	32·71	1·031	4·15
1·285	31·94	1·022	3·03
1·276	31·03	1·014	1·91
1·268	30·13	1·006	0·79
1·257	29·16		

A simple method of determining the strength of phosphoric acid solutions employed in pharmacy, is to transfer the solution to be tested into a graduated flask and to add an excess of N/1 ammonia solution followed by an excess of a saturated neutral solution of magnesium sulphate. The liquid is then diluted to the mark on the flask, well shaken and filtered, and the residual ammonia is then titrated in an aliquot part of the filtrate (Segalle, Zeitsch. anal. Chem. 1895, 33).

Phosphoric acid attacks glass, porcelain, and other silicates, also fused silica at a temperature above 300°, silicyl phosphate and phosphates of the bases being formed. It dissolves ferrochromium alloys, ferro-silicon and spiegeleisen, but the silica of the latter remains undissolved (Byron, J. Soc. Chem. Ind. 1902, 214).

When present in sufficient quantity, phosphoric acid increases the translucency and improves the colour of pottery bodies. It also acts as a flux and vitrifying agent (Parmelee, Trans. Amer. Ceramic Soc. 1906, 8, 236).

Both ortho- and pyro- phosphoric acids form a series of hydrates, those of the latter being less stable and readily passing into the ortho- condition (Giran, Compt. rend. 146, 1270; Smith and Menzies, J. Amer. Chem. Soc. 1909, 31, 1183).

Phosphoric acid possesses three degrees of acidity, the first that of a strong acid, the second that of a weak acid like acetic, the third that of an alcohol, and these correspond with the formation of mono-, di- and tribasic phosphates (Berthelot, Compt. rend. 132, 1277, 1517; Cavalier, *ibid.* 1330), of which the sodium salts may be taken as types. These include the normal or tri-sodium phosphate $Na_3PO_4,2H_2O$, the hydrogen disodium phosphate $HNa_2PO_4,12H_2O$, and the di-hydrogen sodium phosphate

$$H_2NaPO_4,H_2O.$$

The normal alkaline salts are readily soluble and possess an alkaline reaction. The insoluble normal phosphates are converted by dilute acids, even by carbon dioxide, into the soluble hydrogen phosphates. Hydrogen disodium phosphate and corresponding salts are obtained by adding a solution of the hydroxide or carbonate of the base to phosphoric acid until weakly alkaline. The dihydrogen phosphates of the alkalis are soluble and slightly acid. When strongly heated they produce metaphosphates with evolution of water.

The phosphates, which can be freed from phosphoric acid by heating them in a current of chlorine and carbon tetrachloride (Jannasch and Jilke, J. pr. Chem. 1908, [ii.] 78, 21), are, according to Specht and Hutschek (Zeitsch. Farben and Textil. Ind. 1905, 4, 297), very effective as reserves in dyeing processes. This is particularly true of the alkali salts.

When glacial phosphoric acid is heated with glycerol to 100° and the product, after neutralising with barium carbonate and filtering, is decomposed with the calculated amount of sulphuric acid, glycerophosphoric acid is obtained (Porte and Prunier, J. Pharm. Chim. 1894, 393; Adrian and Trillat, *ibid.* 1898, [v.] 7, 226; Compt. rend. 1898, 126, 1215; Bull. Soc. chim. 1898, 19, 684; Imbert and Belugon, *ibid.* 21, 935; Carré, Compt. rend. 1901, 133, 182; 1903, 137, 1070; 1904, 138, 47). Glycerophosphoric acid yields normal and acid salts with the metals and also combines with organic bases such as quinine, cocaine, &c. Phosphoric acid also reacts with mannitol (Carré, *ibid.* 1903, 136, 306).

Phosphoric acid esters can be prepared by stirring together a halogen or fatty acid derivative of a di-glyceride (2 mols.) with phosphorus pentoxide (1 mol.) and water (1 mol.) (Ulzer and Batik, J. Soc. Chem. Ind. 1908, 713; D. R. P. 193189; Arbusoff, Ber. 1905, 38, 1171; Carré, Ann. Chim. Phys. 1905, [viii.] 5, 345; Young, Chem. Soc. Proc. 1907, 65).

Pyrophosphoric acid $H_4P_2O_7$ is obtained by heating orthophosphoric acid to 215° for some time (Giran, Compt. rend. 1902, 134, 1499; 1902, 135, 961; Rosenheim and Pritze, *l.c.*). It occurs either as a soft glass or as an opaque crystalline mass; crystals separate from the syrupy acid at −10° and melt at 61° (Giran, *l.c.*). It may be obtained in solution by precipitating the sodium salt with lead acetate and decomposing the precipitate with sulphuretted hydrogen. When heated in solution it is converted into orthophosphoric acid (Berthelot and André, Compt. rend. 1896, 123, 776; Montemartini and Egidi, Gazz. chim. ital. 1902, 32, i. 381).

Pyrophosphates are obtained by heating the mono-hydrogen phosphates, or by addition of the base to the acid. Both normal and acid sodium and other alkaline pyrophosphates, having an alkaline and an acid reaction respectively, are known. When heated with an acid they are converted into orthophosphates (Ridenour, Chem. Zentr. 1900, i. 834).

Metaphosphoric acid HPO_3 is obtained as a transparent, highly deliquescent glassy mass when orthophosphoric acid is heated until dense white fumes begin to be evolved. It is then known as *glacial phosphoric acid,* and usually contains sodium phosphate, which communicates hardness to the otherwise soft acid (Brescius, Zeitsch. anal. Chem. 6, 187; Bettendorff, *ibid.* 27, 24).

It is also obtained by the spontaneous deliquescence of phosphorus pentoxide.

On standing at the ordinary temperature, or more rapidly when boiled, metaphosphoric acid is changed into the ordinary ortho- acid (Berthelot and André, Compt. rend. 1897, 124, 265; Montemartini and Egidi, Gazz. chim. ital. 1901, i. 31, 394).

Metaphosphoric acid volatilises at a bright-red heat. Its salts are prepared by neutralising the acid or by heating a dihydric orthophosphate. Among the salts no less than five modifications are known. They may be regarded as salts of polymeric metaphosphoric acids, and are respectively known as mono-, di-, tri-, tetra-, and hexametaphosphates.

Various esters, alkyl and other organic derivatives of phosphorus have been prepared (Giran, Compt. rend. 1898, 126, 592; Cavalier, *ibid.* 1898, 127, 60; 1906, 142, 885; Pfeiffer, Ber. 1904, 37, 4620; Rosenheim and Levy, Zeitsch. anorg. Chem. 1905, 43, 34; Hibbert, Ber. 1905, 39, 160; Lemoult, Compt. rend. 1905, 141, 1241; Berthaud, *ibid.* 1906, 143, 1116; Barber, Monatsh. 1906, 27, 379; Anschütz, Annalen, 1907, 358, 92; Michaelis and Linke, Ber. 1907, 40, 3419; Autenrieth and Geyer, *ibid.* 1908, 41, 146; Steinkopf, *ibid.* 3571; Pistschimuka, *ibid.* 385, 4; Levi Malvano, Atti. R. Accad. Lincei, 1908, [v.] 17, i. 847; Swartz, Bull. Acad. Roy. Belg. 1909, 60; Luff and Kipping, Chem. Soc. Trans. 1909, 1993; Arbusoff, J. Russ. Phys. Chem. Soc. 1910, 42, 395).

For detection and estimation of phosphoric acid *v.* ANALYSIS.

PHOTOGRAPHY. Historical. *Introduction.*—Photography is the art by means of which images of various objects may be formed by specially constructed lenses on sensitive films, and there rendered visible and permanent by certain chemical processes.

The effect of light in changing the nature of chemical substances, more especially certain salts of silver, was known to the ancients, but no use was made of such changes until the experiments of Scheele first demonstrated the action of the solar rays on these salts. Count Rumford and Ritter showed that these actions were produced chiefly by invisible rays; but no practical use was made of the discovery of this action of light until Thomas Wedgwood in 1802 published his method of producing sun-pictures on white paper impregnated with a salt of silver.

Daguerre and Niepce, taking advantage of the camera obscura invented by Baptista Porta, succeeded in rendering the images produced by its lenses permanent; and from a long series of experiments devised the process of the Daguerrotype. To Niepce is due the credit of being the first to notice the fact, that the action of light was capable of rendering bitumen insoluble in its ordinary solvents, and that by placing a drawing which had been varnished to make it transparent over a plate covered with a thin layer of bitumen, and exposing the whole to the sun, the parts uncovered by the lines of the drawing could be dissolved away by certain solvents. These early experiments laid the foundation of the modern method of producing copies known under the name of Heliography or Collotype.

A period now followed in which many experiments conducted by Wedgwood, Herschel, and others were carried out on silver compounds; but they proved unsuccessful, chiefly owing to the inability to render the copies made with the silver salts fixed or permanent. Some years afterwards Herschell showed that sodium thiosulphate might be used as a fixing agent, and this substance is employed at the present day. Niepce and Daguerre made experiments on silver iodide as the senstive material. Their experiments resulting in the establishment of the Daguerrotype. In this process a silver plate is treated with iodine, and then exposed in the camera. After exposure it is placed in a properly-constructed box and the image developed by the vapour of mercury. Daguerre was thus able to produce a moderately-sensitive film, and many of the portraits done by the Daguerrotype process still exist in a remarkably good condition.

About the same time Fox Talbot introduced the process known as the Talbotype, in which waxed and iodised paper treated with a silver salt was employed. This paper was more sensitive than the materials previously employed, whereby the exposure necessary was much shortened, the image being developed with gallic acid. These pictures were termed 'negatives' by Talbot, as the lights and shadows were reversed; to produce a 'positive' from these a second sheet of sensitive paper was exposed under the 'negative.' The work of Talbot forms the basis of the more modern processes, and the names of 'positive' and 'negative' introduced by him are still retained.

These inventions were overshadowed by the introduction of the 'wet collodion process' by Scott Archer in 1851, whereby the exposure necessary was reduced to a still shorter time. This process differed from the Talbotype in employing glass as a substratum for the sensitive material, and this, coated with collodion containing the soluble halogen salts, formed the sensitive silver compound by double decomposition on the film. The sensitive plate, being transferred to the camera, was exposed to the light, and the invisible image produced was developed in the dark room in a manner afterwards to be described.

For a long time the wet collodion process held its own; but gradually the advantages to be obtained from a plate sensitised so as to keep without deterioration for some length of time began to be felt, and plates prepared either with a collodion or gelatin emulsion have supplanted, except for certain purposes, the wet plate process. At first dry plates consisted of those prepared in the silver bath, which, after being sensitised and washed, were dipped in some preservative material capable of retaining the sensitiveness of the film for considerable periods. These rapidly gave place to the process now in use, where the sensitive salts, mixed with warm solutions of gelatin, are spread upon glass plates. When dry the plates are ready for use and will apparently keep in a perfect condition for a long period of time. These modern plates differ from the older form of wet plate in being enormously more sensitive, and have thus rendered possible the photography of moving objects and subjects only dimly lighted.

In 1871, R. L. Maddox produced some successful photographs with gelatin emulsion, and a little later they were commercially prepared and introduced for sale by R. Kennett and Burgess. A still more sensitive emulsion was devised by Bennett about 1878, which was produced by prolonged digestion of the prepared mixture at 32°, and finally the discovery that the finished emulsion could be rendered still more rapid by boiling for a short time, or in certain cases by the employment of ammonia in its formation, has given us the numerous and rapid plates which are now to be procured.

In later years the principles underlying the manufacture of sensitive films have not materially altered. The improvements introduced in manufacture and development have largely been in the direction of introducing into the films substances which render them more sensitive to rays of light other than the violet, and thus rendering possible the more modern processes for isochromatic and panchromatic photography.

Apparatus employed.—For a detailed description of the various forms of apparatus employed in photographic work, special text-books must be consulted. There are, however, two important pieces—the lens, and the camera—about which a short description may be given.

The lenses in general use for photographic purposes are: (*a*) single achromatic combination; (*b*) unsymmetrical doublets; (*c*) symmetrical doublets; (*d*) triple combinations; (*e*) anastygmatic combinations; (*f*) telephoto objectives; (*g*) anachromatic combinations. Although the first have been termed 'single lenses,' it must be understood that photographic lenses are combinations of two or more simple lenses, and the term 'single lens' here refers to the fact that only one combination is used, instead of two or more, as in the other or more perfect lenses.

The single lens (Fig. 1) consists generally of a combination of two or more lenses, arranged as a combination in the tube of the lens at the end nearest the camera; the convex side of the combination being towards the plate. This is a good lens with which to begin photographic work. It is fairly rapid with a moderately wide angle, and gives good definition. It is not, however, applicable to the photography of large buildings near at hand, as the marginal rays suffer distortion.

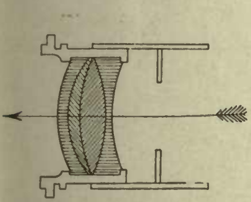
FIG. 1.—SINGLE CONVERTIBLE LANDSCAPE LENS.

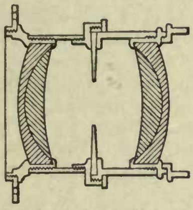
FIG. 2.—RAPID RECTILINEAR LENS.

A rectilinear or symmetrical lens (Fig. 2) consists of two combinations, arranged at the ends of the brass tube, front and back. These combinations are the same in both cases, consisting of a converging meniscus lens cemented to a diverging meniscus, the latter occupying the outside positions in the tube. This is a useful lens, giving practically no distortion and possessing a fairly wide angle.

A symmetrical wide angle lens is constructed much in the same way, and has two combinations formed of meniscus lenses but of much deeper curvature than those employed in other combinations, and placed closer together in the lens tube. Such lenses take in a very wide angle and are specially suited for photographing buildings and portions of landscape in cramped situations. They are somewhat slower than other combinations, but give no appreciable distortion.

The lens for portraiture (Fig. 3) is constructed to get the greatest amount of rapidity, but although possessing that advantage it has some defects. It consists of a back and front combination arranged at some little distance apart. The front combination contains a double convex and a plano-concave lens cemented together, the double convex lens taking the position next the object; the back combination consists of a double convex and a diverging meniscus lens, which are frequently mounted so as to leave a small space between the two lenses. The double convex lens is placed in the tube in the position next the camera.

With the dry plates now obtainable great rapidity can be got with this lens, but it has little depth of focus, poor marginal definition, and presents a rounded field. It is devised for portraiture, and is well adapted to that purpose. In some of the newer lenses constructed on this principle great improvements have been made, diminishing these disadvantages and rendering the lenses useful as universal lenses.

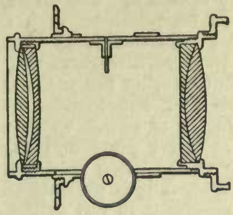
FIG. 3.—PORTRAIT COMBINATION.

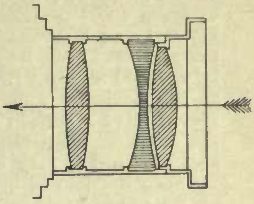
FIG. 4.—COOKE LENS.

Fig. 4 represents the arrangement of the lenses in what is known as the Cooke lens which is much used for hand cameras and in general landscape work. With a wide aperture it covers plates corresponding to the size of the lens well up to the margin, and when stopped down will cover larger plates like a wide angle lens. These lenses are free from distortion and from spherical and chromatic aberration.

Fig. 5 represents the arrangement in the telephoto lens suitable for obtaining views of inaccessible objects.

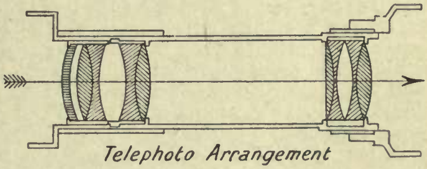

FIG. 5.

The Camera. This consists of a box, made of wood, or, preferably, as in the modern cameras, a framework of wood with a bellows-expanding body of leather, so that when closed the camera may occupy little space and be comparatively light. In front of the camera is placed the lens, and at the back a plate of ground glass, on which the image of the object to be photographed may be focussed, together with an arrangement for lengthening or shortening the body of the camera. The position of the ground-glass screen is the same as that occupied subsequently by the sensitive plate.

Accompanying the camera are one or more double-backed dark slides, arranged to carry two dry plates each, back to back, with a blackened slip of thin sheet iron between them and a sliding shutter, so as to expose the plate when in the camera. In the case of wet-plate work, it is customary to use a dark slide holding only one plate. The dark slides of larger cameras may be fitted with light wooden carriers, which allow of smaller plates being used. For the exposure in the camera of flexible material coated with emulsion other arrangements, such as roller slides, are required, on which the material may be stretched. A description of these will be found under the section describing paper negatives and stripping films. The camera should be made of light and well-seasoned wood, and the body of good leather. It should be capable of opening out to a length two or three times as much as the length of the largest plate it carries. The corners may be brass-bound, especially for cameras required in hot climates. The front, carrying the lens, should be provided with a vertical and a horizontal adjustment, so that the position of the lens in these directions may be changed at will without altering the position of the camera. The back of the instrument should have a certain degree of swing, so that the angle between the sensitive plate and the axis of the lens may be varied when required. By such freedom of movement it is possible to obtain considerable improvement in the adjustment of the forms of objects at different distances and in peculiar positions.

To obviate the necessity of dark backs, cameras have been designed in which a separate slide for the plates is dispensed with, and its place taken by a multiplex back, containing about eight or more plates, which, by a mechanical arrangement, can be alternately exposed to the light. Other more modern cameras have from time to time been introduced where continuous films on rollers may be used.

The support for the camera should be as strong and steady as possible consistent with lightness. For out-door work the camera stand is generally made to fold up, so as to make it more portable, and in most cases the legs of the stand have a sliding adjustment, which is a matter of importance when working on unequal ground. The most important requirement of a stand is perfect rigidity when fixed, so that no vibration may be communicated to the camera during exposure.

Action of light on silver compounds. Although many chemical substances undergo change by light, the halogen compounds of silver are those generally employed in photography, and they may be taken to illustrate such changes, as well as those taking place in the further processes of development and intensification.

Of the composition of the latent image we have no exact knowledge. It is generally accepted, however, that the change, so far as the halogen silver salts are concerned, is the conversion of these into sub-salts, as may be shown by silver bromide, $2AgBr=Ag_2Br+Br$, this change being common to the three halogen salts. Experiments have, however, shown that the change may be probably of a much more complicated kind. Whatever its exact nature may be, there is evidence to show that it will not take place with any facility unless some agent is present which will absorb the halogen as it is liberated during the change. Such agents are to be found in certain metallic salts and in organic substances. In the wet collodion process the presence of excess of silver nitrate on the surface of the sensitive plate acts as such an absorbent. To trace the extent to which such silver compounds, either alone or when mixed, are sensitive to the action of light, the examination must be made by photographing the solar spectrum. This has been extensively done by Abney, Vogel, and many others, and the following general conclusions may be drawn from the experiments :—

The action of the light is different for each of the halogen salts of silver, either alone or when mixed.

It differs also according to the material with which the sensitive compound may be mixed or on which it may be spread, whether at the time of exposure to light the material be in a moist or in a dry condition, and, finally, the different quantities in which the sensitive compounds may be mixed together.

Chemical action in development of the image. As the action of light would have to be immensely prolonged to produce a visible image on the sensitive film, reagents are employed which, exercising a reducing action on the silver salts, render visible the action begun by the light. Such agents are termed developers.

The action which takes place in the development of wet collodion plates, may be illustrated by the action of ferrous sulphate on silver nitrate,

$$6AgNO_3+6FeSO_4=2Fe_2(SO_4)_3+Fe_2(NO_3)_6+3Ag_2,$$

in which it is assumed that the silver so deposited adds itself to the silver salt already changed by the action of the light, and decomposed by the developer, thus :

$$2Ag_2Br+3FeSO_4=Fe_2(SO_4)_3+FeBr_2+4Ag.$$

The developed image in the wet plate is essentially on the surface of the film, because the silver salt is on top of the film. If the ferrous salt and silver nitrate be brought together alone, too rapid reduction takes place. It is customary, therefore, to employ certain substances which act as restrainers during the decomposition. These are to be found in either mineral or organic acids, and in certain other organic compounds.

Development may also be carried out with organic salts of iron, of which the most important is ferrous oxalate :

$$2\,Ag_2Br+3(FeC_2O_4)=Fe_2(C_2O_4)_3+FeBr_2+4Ag,$$

a change comparable with that of the ferrous sulphate just described.

Besides iron salts, pyrogallol is employed, both in the wet-collodion and in dry-plate processes, the action here, as in the case of iron salts, being one of reduction in the presence of some halogen absorbent. In alkaline development the reducing or developing action takes place first on silver sub-bromide, produced by the action of light on the bromide, the bromine thus set free, being absorbed by the organic substratum. In this development the change is produced by pyrogallol rendered alkaline by ammonia or some other alkaline substance, the pyrogallol alone being unable to effect the reduction of the sub-bromide to metallic silver. In the presence of an alkali, however, it becomes a rapid absorbent of oxygen, or of an equivalent of chlorine, bromine or iodine.

As there seems reason to believe that freshly-deposited silver converts unaltered silver bromide into the sub-bromide, and as this sub-bromide, on being attacked by the developer, would at once give a deposit extending over the plate farther than the area of the action of the light, it is necessary to have with the developer some substance capable of acting as a restrainer on the secondary decomposition. Generally, soluble bromides are employed for this purpose, and it is possible that they form a double salt with the silver bromide, less easily attacked by the nascent silver, so obviating a deposit except where the light has begun the action.

It must be understood that our present knowledge of the action of light and of developers on silver salts is not complete enough to enable equations to be written expressing exactly the changes which occur.

The idea of ionisation has been introduced to explain the chemistry of development. Thus in the case of hydroquinone, where it is known that the product formed from it during development is quinone, the hydroquinone is supposed to become ionised, thus losing during the action two negative charges which neutralise the positive charges of the silver in the ionised silver bromide, the oxygen atoms combining to form quinone.

Chemical actions in intensification, reduction, and fixation of negatives. In the process of intensification we have a strengthening of the developed image, which may be brought about in two ways: either by causing a further deposition of silver, or a deposition of some other substance on the silver already deposited during development.

In the first case the change is analogous to that of development. As an instance of the second the following may be taken:

$$Ag_2+2HgCl_2=Hg_2Cl_2+2AgCl, \text{ and}$$
$$Hg_2Cl_2+2NH_4OH=NH_2Hg_2Cl+NH_4Cl+2H_2O$$

when in the first place the silver deposited on the plate, on treatment with mercuric chloride, yields mercurous and silver chlorides. On application of ammonia solution to this, after washing, we have the image darkened by the formation of black dimercurous-ammonium chloride.

Other intensifying agents are employed, of which the following are the most important:—

Mercurous chloride, after washing with sodium sulphite,

$$Hg_2Cl_2+Na_2SO_3+H_2O=2Hg+Na_2SO_4+2HCl.$$

Mercurous chloride with ferrous oxalate,

$$Hg_2Cl_2+2AgCl+4FeC_2O_4+2K_2C_2O_4=2Hg+Ag_2+2Fe_2(C_2O_4)_3+4KCl.$$

Potassio-silver cyanide on mercurous chloride,

$$Hg_2Cl_2+2AgK(CN)_2=Ag_2+2Hg(CN)_2+2KCl.$$

The ferricyanides of lead or uranium on the silver image, $2Ag_2+2Pb_3Fe_2(CN)_{12}$

$$=Ag_4Fe(CN)_6+3Pb_2Fe(CN)_6.$$

The substances formed in this case, being white, are, after washing, treated with an alkaline sulphide to convert them into the dark sulphides. The ferrocyanide of uranium, possessing a dark brown colour, renders the picture sufficiently dense without further treatment.

Fixing the negative. This is generally done with sodium thiosulphate or potassium cyanide, the action of these substances depending upon the formation of soluble double salts of silver with the alkali metals, which can be washed away from the negative. In fixing by sodium thiosulphate, it is necessary that the solution should be concentrated, otherwise an insoluble double salt may be produced. The action in each case may be represented by the following equations:

$$AgBr+2KCN=AgK(CN)_2+KBr$$
$$2AgBr+3Na_2S_2O_3=Ag_2Na_4(S_2O_3)_3+2NaBr.$$

Reducing negatives. It often happens that a negative becomes too dense during the process of development, and it is necessary to reduce its density. This may be done either by mechanical or chemical means. In the application of chemical means two actions may take place, (1) the image may be converted into one of another or less dense colour, or (2) the excess of silver deposit may be removed; the latter is the best course, and is done by transforming the silver into silver chloride or bromide, and removing that by solution. Many substances effect this change, such as cupric and ferric chlorides, bleaching powder solutions, sodium and potassium hypochlorites, ammonium and potassium persulphates. The silver reduces these salts, becoming itself converted into chloride, which may be removed by again fixing.

With copper and ferric chlorides we have

$$Ag_2+2CuCl_2=2AgCl+Cu_2Cl_2$$
$$Ag_2+2FeCl_3=2AgCl+2FeCl_2.$$

These methods have the disadvantage of not showing the full diminution in density till the whole of the AgCl has been removed by the fixing agent. To allow of the final reducing action being seen during the operation, a process has been introduced by which potassio-ferric oxalate is simultaneously used with the sodium thiosulphate

$$Ag_2+Fe_2(C_2O_4)_3=Ag_2C_2O_4+2FeC_2O_4$$
$$Ag_2C_2O_4+3Na_2S_2O_3=Ag_2Na_4(S_2O_3)_3+Na_2C_2O_4$$

(Eder). Potassium ferricyanide may also be employed with sodium thiosulphate

$$2Ag_2+2K_6Fe_2(CN)_{12}=Ag_4Fe(CN)_6+3[K_4Fe(CN)_6]$$
$$Ag_4Fe(CN)_6+6Na_2S_2O_3=2Ag_2Na_4(S_2O_3)_3+Na_4Fe(CN)_6.$$

Preparing and edging plates. To prepare glass plates for coating—either with collodion in the wet-plate process, or for the more modern processes with emulsions—it is necessary, if they have been used before, that all the old film should be removed; and whether they have been used or not, to polish them so as to receive the fresh coating. Old varnished films may be removed by soaking the plates for 24 hours in solutions of hydrochloric or nitric acid containing 1 part of the acid to 20 parts of water. After this time the film can be easily removed by brushing with a nail brush and warm water. After removal of the film the plate should then receive a polish, so that the coating may flow easily over the surface. This is best done with ordinary whiting and water made up to a creamy consistency, or, what has proved very effectual in the writer's experience, rouge made up to the same consistency with alcohol, and a few drops of ammonia added to it to dissolve grease stains. The plate is laid on a pad of thick flannel, a little of the fluid containing the rouge is poured on the plate, which is gently rubbed with a small pad of flannel. The alcohol gradually evaporating leaves the plate covered with a thin film of dry rouge, which is best removed by gently polishing with a pad of tissue paper, the final polish to the plate being given with a second pad. If whiting and water are used, the powder, when dry, must be removed with a slightly-damped cloth, and however perfect the cloth may be, it is apt to leave shreds on the surface of the plate, which may be obviated by using the tissue paper.

When cleaned, it is customary to give the plate an edging or substratum of some material which will assist the collodion or the emulsion to stick more firmly to the plate during the subsequent processes of washing, &c. In dry plates it is not always absolutely necessary to employ an edging, but is sometimes advisable, and is almost imperative with collodion films. The following solutions will be found sufficient for substrata :—

—	*a*	*b*	*c*	*d*	*e*
Albumen	White of 1 egg	Dried 50 grs.	—	—	—
Gelatin	—	—	75 grs.	—	—
Ammonia	5 mm.	5 mm.	2 drs.	—	—
India-rubber	—	—	—	5 grs.	5 grs.
Chloroform	—	—	—	5 oz.	—
Benzene (rectified)	—	—	—	—	5 oz.
Water	60 oz.	50 oz.	60 oz.	—	—

a and *b* must be filtered before use through a light plug of cotton-wool. In *a*, *b*, and *c* the plates may be immersed entirely in the solution, and placed on the rack to dry. In *d* and *e* the solution should be poured on as described for coating with collodion, or an edging of about a quarter of an inch may be given with a brush.

The Collodion Process.

Although gelatin emulsion plates are now extensively used for ordinary photography, collodion plates are still employed in process work, and any account of the subject would be incomplete without a description of this process which for long was the only one in use.

The process depends upon the coating of glass plates with a stratum of soluble pyroxyline or collodion, impregnated with soluble iodides or bromides, which form the sensitive silver compound when placed in a solution of silver nitrate.

The soluble pyroxyline or collodion cotton $C_{18}H_{21}O_6(OH)(NO_3)_8$ is formed by the action of a mixture of nitric and sulphuric acids with a little water (HNO_3 with H_2SO_4 and $1\frac{3}{4}H_2O$), or of a mixture of potassium nitrate with sulphuric acid upon cotton. It differs from cotton in being soluble in a mixture of alcohol and ether, yielding a viscous fluid, which on evaporation leaves the pellicle or film of collodion.

To prepare the soluble cotton for collodion, 3 measured ounces of nitric acid (sp.gr. 1·457) are mixed with 2 ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp.gr. 1·845) are then added to this mixture with constant stirring, and the mixture allowed to cool to 60°. 100 grains of dry cotton, in tufts of about 10 grains each, are immersed in the mixture of acids and allowed to remain from 5 to 10 minutes in a covered beaker. The acid is then poured off, the cotton squeezed with a glass-rod, washed in a stream of water until all acid has disappeared, and finally dried by exposure to the air. Before drying, the cotton may be washed with a little weak solution of sodium carbonate to ensure the total removal of the acid.

The cotton employed must be entirely cleansed of all resinous matter adhering to it. For this purpose it should be boiled in sodium carbonate, thoroughly washed, and finally dried before immersion in the mixed acids.

For larger quantities of pyroxyline the following amounts of the different acids may be taken :

Sulphuric acid, sp.gr. 1·845 . .	18 oz. fl.
Nitric acid, sp.gr. 1·457 . .	6 „
Water	5–5¼ „

The nitric acid is first added to the water, and lastly the sulphuric acid, the mixture being stirred and allowed to cool. These quantities of acid will convert about 300 grains of cotton.

For the manufacture of pyroxyline by the second method with potassium nitrate, the following quantities will be found useful:

Sulphuric acid . . .	6 oz. fl.
Dried potassium nitrate . .	3½ oz. (av.)
Water	1 oz. fl.

The acid and water are first mixed together, and the dried potassium nitrate then added gradually in a finely-crushed condition. On stirring, a transparent viscous liquid is obtained, which must be kept at a temperature of 52°. Into this about 60 grains of dried cotton are then dipped in the manner previously described, and allowed to remain in the mixture for 10 minutes.

To form *collodion* the pyroxyline is dissolved in a mixture of alcohol and ether with the necessary quantities of soluble iodides and bromides to form the sensitive salt when the plate is immersed in the silver bath. The following quantities will give good general results :—

——	i.	ii.	iii.
Pyroxyline . .	120 grs.	120 grs.	100 grs.
Ether, sp.gr. 0·725	10 oz.	10 oz.	10 oz.
Alcohol, sp.gr. 0·805	4 oz.	5 oz.	5 oz.
Ammonium iodide .	30 grs.	40 grs.	50 grs.
Cadmium iodide .	45 grs.	40 grs.	—
Cadmium bromide	—	20 grs.	—
Alcohol, sp.gr. 0·830	4 oz.	5 oz.	5 oz.
Ammonium bromide	—	—	25 grs.

The pyroxyline is first dissolved in the mixed alcohol and ether ; the iodides and bromides are then dissolved in the weaker alcohol and the two solutions mixed. i. gives a simple iodised collodion, ii. a bromo-iodised collodion, both suitable for negatives ; iii. a collodion suitable for positives or ferrotypes.

The sensitising bath. The silver salt employed in the manufacture of this bath is silver nitrate, and the strength for the ordinary bath is from 35 to 40 grains of silver nitrate to the ounce of water except in certain cases. About ⅛th grain of potassium iodide should be added for every 40 grains of silver nitrate ; or the bath may be allowed to become saturated with silver iodide during the subsequent working.

To make the bath, from a quarter to half the quantity of water to be employed is taken, and in it the silver nitrate is dissolved ; to this solution is added the soluble iodide, causing a precipitate of silver iodide gradually dissolving on shaking ; the remainder of the water is then added, the mixture allowed to stand, and filtered. After preparation the bath should be slightly acid, and for this a drop or two of nitric or acetic acid may be added, preferably the former. Should the bath be too acid after making, a little sodium carbonate may be added. The following are convenient quantities for the preparation of larger amounts of bath solution—

	For negatives	For positives and ferrotypes
Silver nitrate (recrystallised)	6 oz.	5 oz.
Distilled water . .	80 oz.	80 oz.
Nitric acid . . .	10 min.	12 min.

Saturate with an iodide as before described, and filter.

Development of the latent image. The chemistry of the action of the wet plate process has been already indicated. It is only necessary now to give formulæ best adapted to the development of the image. Those relate particularly to the acid development collodion process.

The following table gives the quantities necessary for some useful iron developers for wet plates :—

——	*a*	*b*	*c*	*d*
Ferrous sulphate	75 grs.	180 grs.	100 grs.	—
Ammonio-ferrous sulphate .	—	—	—	125 grs.
Copper sulphate	—	—	50 grs.	—
Barium nitrate[1]	—	120 grs.	—	—
Acetic acid .	120 min.	120 min.	100 min.	125 min.
Alcohol . .	120 ,,	—	100 ,,	125 ,,
Nitric acid .	3 ,,	10 min.	—	—
Water . .	5 oz.	5 oz.	5 oz.	5 oz.

In the wet-plate process the development may be carried out by pouring a sufficient quantity of the fluid over the plate, or the plate may be immersed in a dish as in the case of dry plates. When sufficient detail has made its appearance, the excess of developer is washed off by a stream of water.

Intensification of wet plates. When the density of the negative is not sufficient for printing purposes, it may be strengthened by pouring over the plate a sufficient quantity of either of the following solutions :

	a	*b*
Pyrogallol . . .	10 grs.	—
Citric acid . .	20 grs.	50 grs.
Ferrous sulphate .	—	25 grs.
Water . . .	5 oz.	5 oz.

After the plate has been thoroughly moistened with the solution, the latter is poured back into the developing-glass and a few drops of a 10-grain solution of silver nitrate added to it. On re-flooding the plate with the mixture, the image will gradually gain in density. Other substances may be employed as intensifiers, some of which will be mentioned in connection with dry plates, but for a full description of the various formulæ text-books on photography must be consulted.

Fixing. To remove the unacted-upon silver salt, sodium thiosulphate or potassium cyanide may be employed; the solution being contained in a flat dish, or in an upright bath provided with a dipper. The following quantities are those generally employed for plates—

	a
Sodium thiosulphate . .	4 oz.
Water	20 oz.

	b
Potassium cyanide . . .	120 grs.
Water	5 oz.

a is preferred for negatives, *b* for positives. Great care is required in the employment of the latter salt on account of its very poisonous character.

Varnishes.—For the protection of films they should be covered with a coating of varnish as clear and as hard as possible, to prevent damage during the operation of printing. These varnishes are resins dissolved in such solvents as alcohol, benzene, or chloroform. The composition of some of these is kept secret, but the quantities given in the next column yield good material for ordinary work.

a and *c* are suitable for negatives, *c* being very hard and durable. *b* may be rubbed off for retouching the negative, and should not be used when great permanency is required. For further details with regard to photographic varnishes *v.* VARNISH.

——	*a*	*b*	*c*	*d*
Shellac . .	150 gr.	—	—	—
Sandarac . .	150 ,,	384 gr.	—	430 gr.
Mastic . .	60 ,,	—	—	—
White hard varnish	—	—	3 oz.	—
Camphor . .	3 gr.	—	—	—
Oil of lavender .	—	5 dr.	—	1 dr.
Chloroform .	—	2 ,,	—	—
Oil of turpentine .	½ dr.	—	—	3 dr.
Venice turpentine	½ dr.	—	—	—
Alcohol . .	5 oz.	5 oz.	5 oz.	5 oz.

DRY PLATE PROCESSES.

Collodion emulsion. Next to the wet plate process come the more modern or emulsion processes, which may conveniently be divided into those containing collodion, and those containing gelatin as the thickening medium in the emulsion. Gelatin emulsions are now the most important; but, the others being useful for certain purposes, the production of a collodion emulsion is briefly described before proceeding to those in which gelatin is employed.

The plates having been prepared and edged, if necessary, as previously described, may be coated with an emulsion prepared in the following manner. The plain collodion may be made by dissolving 200 grains of ordinary pyroxyline in 5 ounces of alcohol (sp.gr. 0·820) mixed with 10 ounces of ether (sp.gr. 0·730). To make, say, 1 pint of emulsion from this, after the final treatment of emulsification, drying, washing, and re-emulsifying has been gone through, we may take 7½ ounces, or the half of the collodion prepared. 200 grains of zinc bromide are next weighed out in two portions of 100 grains each, one of these portions being dissolved in the smallest quantity of alcohol; 4 or 5 drops of nitric acid are added to the solution, and then poured into the collodion. The second 100 grains are dissolved in a boiling tube in alcohol, 10 drops of nitric acid added, and kept ready for use. Next 330 grains of silver nitrate are weighed out and dissolved in about 5 to 6 drs. of water, and 10 drops of nitric acid added to the solution. To this solution 1½ ounces of warm alcohol are added, and the two liquids thoroughly mixed. The collodion containing the zinc bromide is now placed in a vessel convenient for mixing, and the solution of silver nitrate gradually added, with constant stirring, till about one-half to three-quarters of the silver solution has been poured in. The whole of the bromide solution is now added in exactly the same way as described, and then the remainder of the silver solution. Should any of the silver solution crystallise on the sides of the boiling-tube it may be dissolved in a little water and about half an ounce of alcohol, and added to the emulsion with constant stirring. The emulsion so prepared, when examined by a candle or gas flame, should appear of a deep orange tint by the light transmitted through a thin film.

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[1] The insoluble barium sulphate formed is filtered off; *b* is suitable for positives.

Manufacture of gelatin emulsions. Gelatin emulsions are now so varied in their nature and the details of their special preparations are so carefully guarded by the different makers, that it is impossible here to deal with the details of their preparations. Only a short description is given, therefore, of the general points in the manufacture of an emulsion on a small scale.

Gelatin emulsions may be arranged in the following three classes: (*a*) the ammonio nitrate process, (*b*) the acid boiling process, and (*c*) the cold process. (*a*) is simple, easy to perform and suitable for beginners; (*b*) requires more apparatus and does not yield quite so sensitive an emulsion; (*c*) requires no heating but is apt to yield irregular results.

It is necessary that all operations in making the emulsion—heating to obtain the required rapidity, and finally washing the emulsion when formed—should be carried out in the dark room or in red light. For most cases, light passing through ruby glass is sufficient, but in the manufacture of extra rapid emulsions greater precaution with regard to light is necessary. As during the process of manufacture the emulsion must be kept at a certain temperature, glass or porcelain vessels are necessary for dissolving and mixing the constituents, and a small pan or dish is required for keeping these vessels at the required temperature by hot water.

The substances required for a simple emulsion are silver nitrate, potassium bromide, and autotype, or hard gelatin. Convenient quantities for a small amount of emulsion are obtained by taking 300 grains of gelatin, cut up into shreds by scissors. These are transferred to a glass beaker, or other vessel, and covered with 5 ounces of water, in which 185 grains of potassium bromide have previously been dissolved. By a little manipulation with a glass rod the gelatin gradually softens and swells. While the gelatin is being softened, 231 grains of silver nitrate are dissolved in 5 ounces of water by gentle heat in the pan or water-bath, and when the solid is thoroughly dissolved some strong solution of ammonia (0·880) is gradually added to the silver solution, with constant stirring, until the precipitate which first forms is dissolved. The two vessels are now placed in a pan with water, kept rigorously at a temperature never rising above 35° until the gelatin becomes first viscous, and then, with constant stirring, perfectly liquid. It is essential that the gelatin be perfectly liquid before adding the silver salt. Up to this point the operations may be carried out in the ordinary light, but all further work must be done in ruby light.

When the gelatin is thoroughly liquefied the solution of silver nitrate is added gradually with constant stirring. Many arrangements have been devised from time to time for the proper addition of the silver solution to the gelatin, but it can be done with ease by pouring the solution in a thin stream from an ordinary lipped beaker, or through a glass funnel with a very small orifice. When the mixture is complete, wash out the rest of the silver solution remaining in the beaker with about an ounce of warm water, and add to the emulsion. The emulsion must now be examined by spreading a little on a glass plate and looking at it by transmitted light, when it should appear of a violet colour, apparently with a tendency to assume a rose-pink tinge. The emulsion having been allowed to remain in the hot water for from half to three-quarters of an hour to undergo a process of ripening, it is then poured into a flat photographic dish, placed in a perfectly dark box, and allowed to set. It should remain thus for at least 24 hours, but will be better if allowed to remain two or three days. As the emulsion when first prepared contains an excess of silver salt, it must undergo a process of washing, which may be carried out in ruby light in two ways.

The gelatine pellicle, having been scraped off from the dish by a bone or glass spatula, is transferred to a square of coarse canvas, thoroughly wetted to soften it. The corners of the square are gathered together and tied with string, thus inclosing the pellicle in a rough bag. This bag, containing the pellicle, is placed in a vessel of water, and thoroughly kneaded by squeezing it against the sides of the vessel by means of the spatula. The pellicle is thus squeezed in threads through the canvas, and falls to the bottom of the washing vessel. When the whole of the emulsion has been thus treated, the water is poured off and the pellicle again covered with fresh water, allowed to stand for about 5 minutes, and the water again poured off, this operation being repeated six or eight times. It will be found advantageous during the process of washing to tease up the shreds of pellicle. Where a tap and running water can be obtained, the washing will be facilitated.

After perfect washing the pellicle is turned out of the washing jar on to a porcelain strainer, covered with a handkerchief, and the excess of water drained away. It may then be swilled with a wash of methylated spirit, which facilitates drying, and transferred by the porcelain spatula or glass spoon to a suitable jar covered with a lid, until it is required for coating the plates. Other methods of washing the pellicle have been introduced, such as placing it on a hair sieve after squeezing through canvas, and then washing on the sieve in a stream of water from the rose tap. It is possible that spreading the emulsion on a sieve facilitates the subsequent drying.

A second method of washing the emulsion and removing the soluble salts is to precipitate it with alcohol. This is done by pouring warm methylated spirit into the emulsion, with constant stirring, when, on allowing the mixture to cool, the emulsion is found precipitated at the bottom of the vessel. The precipitated emulsion can then be washed in a stream of water, and transferred to a covered pot until required for coating the plates.

The numbers just given will be found convenient for a beginner making an emulsion for the first time, and yield one of moderate rapidity. The following table gives a selected series of emulsions suitable for different purposes. Nos. I. and II. are of different degrees of rapidity, the first yielding a material suitable for landscapes, when no great rapidity is required: the second deals with an emulsion of greater sensitiveness.

TABLE OF VARIOUS GELATINO-BROMIDE EMULSIONS.

	——	I.	II.	III.	IV.	V.	VI.
A	Silver nitrate	200 grains	200 grains	400 grains	200 grains	330 grains	462 grains
	Distilled water	3 ounces	3 ounces	7 ounces	3 ounces	3 ounces	10 ounces
	Ammonia (·880)	—	—	sufficient to dissolve ppt.	—	—	sufficient to dissolve ppt.
B	Ammonium iodide	—	—	24 grains	—	—	—
	Ammonium bromide	—	—	280 grains	120 grains	200 grains	—
	Potassium bromide	160 grains	165 grains	—	—	—	370 grains
	Gelatin (Nelson's No. 1)	40 grains	30 grains	80 grains	30 grains	218 grains	615 grains
	Hydrochloric acid (1 p.c. sol.)	200 mins.	—	—	—	—	—
	Distilled water	2½ ounces	2½ ounces	5½ ounces	4 ounces	3 ounces	10 ounces
C	Potassium iodide	12 grains	6 grains	—	—	—	—
	Distilled water	½ ounce	½ ounce	—	—	—	—
D	French gelatin	—	—	—	—	218 grains	—
	Hard gelatin	300 grains	250 grains	—	200 grains	—	—
	Water	4 ounces	3 ounces	—	—	3 ounces	—
E	Methylated spirit	—	—	2½ ounces	—	—	—
	Salicylic acid	—	—	25 grains	—	—	—

For more detailed information regarding the manufacture, ripening, &c., of gelatin emulsions the various text-books on photography must be consulted.

For coating ordinary-sized plates with emulsion on a small scale the following method may be employed. The plate must be laid on a very accurately-levelled stand or tripod. A quantity of emulsion sufficient to cover nearly half the plate is poured on the middle of it: a glass rod about 2 ins. longer than the width of the plate is then grasped between the fingers and thumbs of both hands, dipped across the plate, into the middle of the pool of emulsion, and steadily moved first to one end and then to the other of the plate. By a motion of the finger and thumb the rod can be raised a slight distance from the plate, so as to allow the emulsion to coat smoothly, and, by resting the tips of the finger and thumb upon the levelled slab, a guiding motion may be given to the rod. In the large manufactories many mechanical arrangements are employed to facilitate rapid coating of the plates.

When the emulsion is thoroughly set on the plates, they are removed from the level slab to a suitable rack to undergo a thorough drying process. This is most conveniently done in a specially-constructed drying-box with a current of air artificially heated from the outside passing through it. The artificial heating of the air is unnecessary if the air-passages are sufficiently large and properly arranged.

The plates will take from 12 to 48 hours to dry, according to circumstances, and may then be packed until required for use.

Ortho-chromatic photography. On comparing the curves indicating the intensities of the visual and the photographed spectrum, it will be at once observed that very little relation exists between them, the visual intensity being greatest about the points D and C, and the photographic intensity about the point G in the spectrum, gradually diminishing to the points marked F and E (Fig. 6).

The object of ortho-chromatic photography is by the use of certain dyes introduced into the sensitive material to bring the visual and the photographic intensity as much into harmony as possible. This unison may be partially brought about by the introduction into the photographic film of substances such as eosin, erythrosin, rose of Bengal, cyanin, &c.

The most important work in the direction of ortho-chromatic photography has been carried out by Becquerel, Eder, and Vogel on the continent; Cary Lea in America, and by Abney, Waterhouse, and C. H. Bothamley in this country. The dyes are now generally incorporated with the sensitive film, but may also be used in the form of screens placed in close juxtaposition to the plate.

The amount of dye employed must be small, as the effect is destroyed by large quantities. When mixed with the emulsion it is generally found best to employ about 15–30 min. for every 500 c.c. of emulsion; but when the sensitive plate is dipped in the dye a solution of 1 part of dye in 20,000 of water is sufficient.

Orthochromatic plates may be divided into (1) those sensitive to the green and yellow rays, (2) to orange and red rays, and (3) to the entire spectrum (panchromatic). There are many sensitive substances employed, but the following table shows some of those most commonly used :—

——		*a*	*b*	*c*
I.	Erythrosin	10 grs.	—	—
	Cyanine blue (ethyl cyanine or pinacyanol)	—	1 gr.	—
	Auracine	—	—	1 gr.
	Alcohol	4 oz.	8 oz.	—
	Water	—	—	10 oz.
II.	Ammonia (0·880)	1 dr.	—	1 dr.
	Water	24 oz.	—	—

(*a*) is suitable for the green-yellow region, and if the plate be coated with the sensitiser by dipping, it should be used within a few days. (*b*) is for the red region. These plates from their sensitiveness must be prepared practically in the dark. (*c*) is for green and blue-green rays. The auracine is dissolved in boiling water, filtered, and the ammonia added to the cooled solution. This solution reduces the speed of the plate.

For panchromatic plates the two following solutions may be used : (*d*) alcoholic solution of pinachrome (1 : 1000) ; ammonia (0·880), 5 min. ; water, 1 oz. ; (*e*) alcoholic solution of homocol (1 : 1000) ; ammonia, 10 min. ; water, 1 oz.

Special care must be taken in preparing these plates, which should be done somewhat quickly, and in the dark.

Many other sensitisers may be used, of which the following are instances. For blue-green and green, acridine orange without ammonia. For green and yellow (but not red) erythrosin as above. Green, yellow and red, orthochrome, pinaverdol, pinachrome or homocol. Extreme visible red, pinacyanol. Infra-red, dicyanine.

The following curves, taken from Bothamley's papers on this subject, show the increased sensitiveness produced by some of these dyes in the portion of the spectrum lying between A and E :—

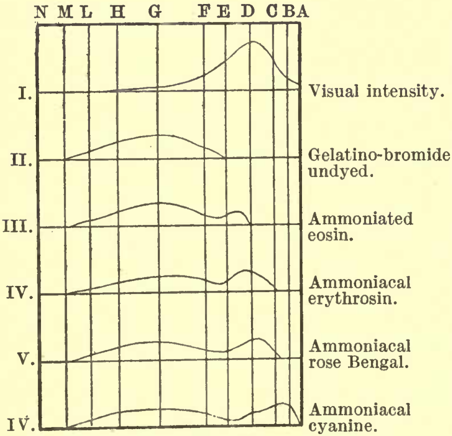
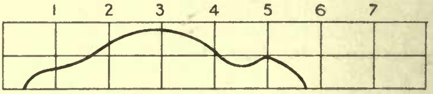


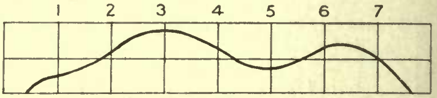
FIG. 6.

The following diagrams indicate the increased sensitiveness of (*a*) an isochromatic plate showing partial sensitiveness ; and (*b*) a panchromatic plate with the sensitiveness extending into the red rays.



Spectrum of Isochromatic Plate

FIG. 7(*a*).



Spectrum of Panchromatic Plate

FIG. 7(*b*).

The chief use for plates so sensitised will be found in the copying of pictures, flowers, or distinct patterns of different colours, where as much harmony as possible is required between the visual and photographic effect, but they will also prove useful in harmonising contrasts sometimes found in portraiture.

For detailed information on ortho-chromatic photography special papers relating to the subject should be consulted.

DEVELOPMENT OF DRY PLATES.

The development of dry plates produced either by collodion or gelatin emulsion is carried out either by iron-salts—such as ferrous oxalate or ferrous citro-oxalate—or by what is termed 'alkaline development,' in which pyrogallol, hydroquinone, amidol, or some other organic-reducing agent, associated with the bromides of potassium or ammonium as retarders, and with ammonia, or the carbonates of potassium or sodium, as accelerators of the reducing action.

Development with ferrous oxalate. This method is simple for ordinary dry plates, and may be employed for negatives on paper, or enlargements on gelatino-bromide paper, but it does not permit correction of inaccurate exposure to such an extent as the pyro-developer. The ferrous oxalate developer may be prepared by adding 1 volume of a saturated ferrous sulphate solution to 4 volumes of a saturated solution of potassium oxalate. Such solutions are obtained by dissolving 4 oz. of neutral potassium oxalate and 6 oz. ferrous sulphate separately, each in 10 oz. of water. A solution of potassium bromide, containing 20 grs. bromide to the oz. of water, should also be made ; of this, about 4 drops should be taken for every 2½ oz. of developer. The ferrous oxalate developer is specially applicable in the development of transparencies or positives made with gelatino-chloride or collodio-chloriodo emulsions. It is, however, generally found better for this last-named emulsion to employ a ferrous-citro-oxalate, or ferrous citrate developer, with which, by varying the amount of the accelerator, graduated tones may be given to the transparency. The quantities given in the following table may be regarded as good standard quantities to be selected from :—

For Transparencies.

	——	a	b
I.	Potassium oxalate	5 oz.	2 oz.
	Ammonium chloride	—	40 grs.
	Citric acid	—	—
	Water	20 oz.	20 oz.
	Ferrous sulphate	5 oz.	240 grs.
II.	Sulphuric acid	30 mm.	—
	Citric acid	—	120 grs.
	Alum	—	120 grs.
	Water	20 oz.	16 oz.

With (*a*) mix 1 oz. of I. with 3–4 oz. of II., pouring II. into I. To obtain black tones with (*b*) use equal proportions of I. and II. The solutions when mixed may be used for several plates in succession.

Development by ferrous oxalate or ferrous-citro-oxalate is simpler than with alkaline pyrogallate, but greater attention must be paid to the exposure, as there is less power of working up an under-exposed plate.

Alkaline development.—In this development the pyrogallol gives density, the soluble bromide is supposed to act as a restrainer, and the ammonia or alkaline carbonate as an accelerator. The pyrogallol may be kept in the dry condition and added to the developer when required, but it is customary to keep all the substances as separate stock solutions. For perfect work it is therefore better to keep the three ingredients separate, but the stock solutions may be reduced to two in number, and even a single stock solution may be used. In this latter case, however, the operator has not so much control over the retardation or acceleration of the development in cases of incorrect exposure. The amount of pyrogallol generally employed varies from between 1 grain to 5 grains per fluid ounce of developer, and full details of the correct quantities are almost universally given with the plates supplied by the different makers.

Developing solutions for gelatino-bromide plates. The following may be taken as instances of standard forms of developers. The solutions should preferably be kept separate, at least the organic developer should not be mixed with the alkali till required for use. I. may be termed the developer; II. the accelerator; and III. the restrainer, to be used if required in over-exposure. The following developers with pyrogallol are given as types of the two and three solution developers.

	——	a	b
I.	Pyrogallol	1 oz.	¼ oz.
	Nitric acid	—	5 min.
	Citric acid	40 grs.	—
	Water	7½ oz.	20 oz.
II.	Ammonia solution (0·880)	1 oz.	—
	Sodium sulphite	—	2½ oz.
	Sodium carbonate	—	2 oz.
	Potassium bromide	120 grs.	—
	Water	7 oz.	20 oz.
III.	Potassium bromide	—	¼ oz.
	Water	—	2 oz.

(*a*) In separate bottles take 1 part of No. I. and of No. II., and to each add 19 parts of water. These should be mixed just before use. To develop when the exposure is correct take equal parts of the diluted solutions.

(*b*) Mix equal parts of Nos. I. and II., and add 10 min. of No. III. to each ounce of the mixed developer. For instantaneous exposures No. III. may be omitted.

The manipulation required in dry plate development is very simple, as the operation is carried out in a dish. The plate, taken from the dark slide, is laid in the developing dish or tray face upwards, and if ferrous oxalate or citrate be used the proper quantity may at once be flowed over the plate, allowing the liquid to run gently from one end of the plate to the other. A gentle rocking motion may be given to the dish during development, so as to change the liquid over the surface of the plate. The image gradually appears, the high lights gaining density first. Complete development may be recognised by a faint image appearing on the back of the negative, or looking through the negative at the red window or lamp, when the plate should show a very complete deposition of silver on the high lights. The knowledge of the exact extent for correct development can only be obtained by practice.

Table of some of the Common Developers.

	——	a	b	c	d
I.	Pyrogallol	55 grs.	80 grs.	—	
	Metol	45 grs.	—	—	—
	Hydrodinine	—	8 grs.	40 grs.	120 grs.
	Eikonogen	—	—	120 grs.	—
	Potassium meta-bisulphite	120 grs.	80 grs.	—	—
	,, bromide	20 grs.	—	—	60 grs.
	Sodium sulphite	—	—	1 oz.	1 oz.
	Citric acid	—	—	20 grs.	5 grs.
	Boric acid	—	10 grs.	—	—
	Water	20 oz.	20 oz.	20 oz.	20 oz.
II.	Sodium carbonate	4 oz.	1 oz.	60 grs.	—
	,, hydroxide	—	—	30 grs.	—
	Potassium bromide	—	—	6 grs.	—
	,, carbonate	—	—	—	2 oz.
	Rodinal	—	—	—	1 oz.
	Sodium sulphite	—	1 oz.	—	—
	Water	20 oz.	20 oz.	20 oz.	20 oz.

In many cases the organic developer and the alkaline accelerator may be mixed together in one solution. The following may be taken as typical developers of this class :—

	——	*a*	*b*	*c*	*d*	*e*	*f*	*g*
Organic Developers.	Eikinogen	120 gr.	—	—	—	—	—	—
	Glycin	—	160 gr.	—	—	—	—	—
	Hydroquinone	—	—	50 gr.	65 gr.	—	25 gr.	—
	Formalin	—	—	—	1½ dr. fl.	—	—	—
	Metol	—	—	—	—	75 gr.	18 gr.	—
	p.-Aminophenol	—	—	—	—	—	—	480 gr.
Accelerators.	Sodium carbonate	240 gr.	—	720 gr.	—	840 gr.	360 gr.	—
	,, sulphite	480 gr.	240 gr.	360 gr.	1440 gr.	600 gr.	480 gr.	—
	Potassium carbonate	—	800 gr.	—	—	—	—	—
	,, bromide	—	—	—	—	8 gr.	—	—
	,, metabisulphite	—	—	—	—	—	—	1440 gr.
	Water	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.	10 oz.

As a rule these developers should be diluted with an equal quantity of water immediately before developing. With developer (*e*) for portraits take equal parts of stock solution and water; for landscapes 1 part of stock to 2 of water.

The glycin developer (*b*) is a slow developer, but particularly suitable for 'stand development.'

In commencing the development of a plate it is better to begin with a less quantity of the accelerator than the full amount stated, and gradually add the remainder as development advances.

The darkening of the film when the alkaline pyrogallol developer is used must not be allowed to go on so long as with the ferrous oxalate developer. In the former case the image is of a slightly yellow tinge, and consequently of a more non-actinic nature than that formed by the oxalate. As has been already stated it is not absolutely necessary that three separate solutions be kept, but this course is better so as to facilitate the retardation of development on over-exposure, or its acceleration on under-exposure. If proper exposure has been given the image will appear in about one minute, and gradually gain in strength. When all the details are visible, and the development apparently stops, a few more drops of the accelerator may be poured into the developing cup, the developer mixed with it, and again flowed over the plate. This fresh addition of the alkali rapidly produces increase of density. When the development is deemed complete, wash thoroughly in a gentle stream of water from the rose-tap and place in the fixing-bath, unless it be deemed necessary to soak the plate in an alum solution to prevent frilling.

For the special development of dry plates for *transparencies*, or slides to be used in the lantern, the developers given in the following table will be found useful, and will give different tones to the transparencies :—

Pyro and Ammonia Developer for Warm Tones.

I.	Pyrogallol	1 oz.
	Sodium sulphite	4 oz.
	Citric acid	¼ oz.
	Water	16 oz.
II.	Ammonium bromide	1 oz.
	Liquor ammonia (0·880)	5½ dr.
	Water up to	16 oz.

For use mix 1 part of No. I. with 3 parts of No. II. and dilute to double the quantity with water. The mixed developer may be used for several plates.

Developers for Black Tones.

——	*a*	*b*
Hydroquinone	60 grs.	—
Amidol	—	80 grs.
Sodium carbonate	4 oz.	—
,, sulphite	2 oz.	2 oz.
Potassium carbonate	2 oz.	—
,, bromide	40 grs.	½ oz.
Water	20 oz.	12 oz.

These developers may be used for several plates, and will keep good for some time. In almost all cases it will be found best to use the developer which is generally described on the box of the special plate used.

Many operators now prefer a fixed time development during which the plate if properly exposed need not be examined. This is carried out in a closed box or tank, of which many forms are on the market. Tables are also given by which the time necessary for different developers may be calculated.

Intensification and reduction of dry-plate negatives. If proper exposure be given to the plate the process of development by the ferrous salt or by pyrogallol will always yield sufficient printing density. Both under- or over-exposure, however, will yield an image far too thin to give a vigorous and brilliant print. This deficiency may be remedied to a certain extent by the process of intensification; but it must be understood that the results, when such a process has to be employed, are never so brilliant as with a properly-exposed and properly-developed negative.

Several methods are in general use for the intensification of dry plates, one of the most usual being that in which the action is carried out by a mercury salt and ammonia. In dry plate work the process of intensification is almost invariably carried out after fixing. For this purpose it is necessary that the last traces of sodium thiosulphate should be removed from the negative by thorough washing. Should it be necessary to take still further precautions for the removal of the last traces of thiosulphate, the negative should be soaked in a saturated solution of alum containing 3 grains of citric acid to the ounce of solution, or in a solution of hydrogen peroxide containing 1 drachm of 'hydrogen peroxide solution' to 5 oz. of water. The plate may be soaked in these from 10 to 30 minutes, and again washed before intensification.

To intensify, first thoroughly soak the plate in water to soften the film, then place in the following solution, preferably in a black vulcanite dish :—

I.

Mercuric chloride . .	200 grs.
Ammonium chloride . .	200 grs.
Water	10 oz.

The plate rapidly undergoes a process of bleaching, and when the film is bleached throughout it is removed from the solution and thoroughly washed under the tap. The washing in this case must be most thorough. After this washing the plate is flooded with a solution of ammonia :

II.

Ammonia, 0·880 . . .	1 part
Water	10 parts

In this solution the plate rapidly assumes density, becoming changed first to a rich non-actinic brown, and finally to black, according to the length of time it has been left in the mercury bath.

The plate may also be intensified by one or other of the following solutions :—

——	*a*	*b*	*c*	*d*
Sodium sulphite	1 part	—	—	—
Ferrous oxalate	—	ordinary developer	—	—
Hydroquinone .	—	—	ordinary developer	—
Uranium nitrate	—	—	—	1 part
Potassium ferricyanide .	—	—	—	1 ,,
Acetic acid (glacial)	—	—	—	10 parts
Water . .	6 parts	—	—	100 ,,

(*a*), (*b*), and (*c*) are to be used after the negative has been bleached by the mercuric chloride solution ; (*d*) is an intensifier by itself.

In all cases the plates should be well washed between the application of solutions I. and II. and after intensification ; they may also be placed in the fixing bath again for a minute or two with advantage, and then finally washed.

Reducing negatives. Should the negative after development and fixing appear too dense for printing purposes, one of the following courses of treatment will cause its reduction :—

(1) Soak the plate carefully in sodium thiosulphate solution (2 oz. to 1 pint) to which has been added potassium ferricyanide sufficient to give it a yellow colour. The reduction in this case takes place with considerable rapidity, and a stream of water or a washing dish should be handy for immersion of the negative to check too rapid reduction.

(2) Immerse the moist negative in one of the following solutions :—

——	*a*	*b*	*c*	*d*
Potassium ferric oxalate	150 grs.	—	—	—
Sodium sulphite . .	125 ,,	—	—	—
Oxalic acid . .	45 ,,	—	—	—
Sodium thiosulphate .	1¼ oz.	—	—	—
Ammonium persulphate	—	15 grs.	—	—
Potassium permanganate (10 p.c. solution)	—	—	1 dr.fl.	—
Potassium dichromate	—	—	—	100 grs.
Sulphuric acid (10 p.c. solution) . . .	—	—	5 dr.fl.	7 dr.fl.
Water . . .	7 oz.	1 oz.	10 oz.	20 oz.

Fixing the negative. This operation is practically the same for dry plates as has already been described for wet plates, except that sodium thiosulphate is always employed and not potassium cyanide. The usual strength of the solution is 4 oz. of thiosulphate to 1 pint of water, but this may be varied according to the experience of the operator.

Transparencies. When a positive picture is required for enlargement, or for showing on a screen to an audience, it is found more convenient to employ an emulsion of gelatin and silver chloride, alone or a mixture of the silver chloride and bromide. The following quantities may be taken as giving emulsions suitable for this purpose :—

	——	I.	II.
A	Gelatin (Nelson No. 1) .	300 grs.	80 grs.
	Ammonium bromide .	—	210 grs.
	Ammonium chloride .	100 grs.	—
	Sodium chloride . .	—	50 grs.
	Hydrochloric acid .	—	5 mm.
	Water	10 oz.	10 oz.
B	Silver nitrate . .	240 grs.	400 grs.
C	Hard emulsion gelatin .	—	400 grs.

In No. 1 allow the gelatin to soften and swell in the water ; then place all three vessels in a water-bath at a temperature of 120°F. (49°C.). When the gelatin is melted add the silver solution to it, and then stir in the ammonium chloride solution. Allow the emulsion to ripen at that temperature for an hour, and pour out into a dish for setting. The details of washing, coating, and drying the plates, are the same as for the bromide emulsions already described.

As the film left by gelatino-chloride plates after development and fixing is extremely clear in the high lights, it is necessary for these plates to employ glass perfectly free from flaws or air bubbles.

Gelatino-chloride plates are less sensitive to light than the bromide plates, so that for contact transparencies from well-defined negatives, the exposures are proportionately longer.

These plates may be developed by ferrous oxalate, or by the mixture of ferrous oxalate and citrate previously mentioned, or by the hydroquinone developer.

Gelatino-bromide plates also yield good transparencies, but if they are used for this purpose a fairly strong pyro-developer should be taken and the development carried out quickly.

Transparencies are now commonly made by sensitive carbon tissue (*v. Carbon processes*).

Formulæ useful in the development of transparencies are described under the development of gelatin-plates.

Negatives on paper or celluloid films. In the earliest form of negative—that introduced by Fox Talbot—the material employed as the substratum for the sensitive film was paper instead of glass. Although the employment of glass as a support to the sensitive film became generally adopted when the collodion process was perfected by Archer in 1852, paper and particularly celluloid material have again come into use. This reintroduction of paper as a basis for the sensitive film is due in a great measure to Messrs. Woodbury and Warnerke, who have acted as pioneers in this, and in the design of apparatus necessary for the manipulation of such coated surfaces.

The details of coating such films with the emulsion are nearly allied to those of coating the glass plate. The actual difference between the two methods consists in the special manner in which the sensitive films are arranged in the camera for exposure. This may be done in two ways. The film, if sufficiently rigid, may be cut into definite sizes the same as the glass plates, and then fixed by specially-constructed slips of thin wood or metal in the ordinary dark slides exactly in the position that would be taken by the glass plate. Another method is to suspend the sensitive paper in a continuous roll in what is termed a roller slide, which takes the place of the dark slide containing the sensitive plate. In this arrangement the continuous slip may be rolled off from one spool to another across the camera, a mechanical check or signal being given as soon as the length of paper corresponding to the width of the camera has passed over, thus placing a fresh surface in position before the lens. The process may be repeated until twelve or more portions of the continuous film have been exposed. The film may then be removed from the dark slide for development, and another roll placed on the rollers in the slide.

The development of such films may be carried out with the same solutions as those employed for glass-plate development. Should the film be thick enough they may be treated as glass plates, but under ordinary circumstances the films now used are too thin for such treatment and are best developed as a whole film. For this purpose the film may be attached to a roller or wheel which can be rotated in the developer; or the film may be held at each end by the hand and passed through the developer backwards and forwards with the sensitive side downwards, being kept down in the developer by a porcelain bridge standing in the developing dish. It will be found advantageous to soak the paper in water before development until all tendency to curl up has disappeared. Retardation or acceleration of the development may be done in the same manner as for glass plates.

Various appliances, such as developing tanks, have been introduced of late years for the development both of plates and roller films, which have removed many of the difficulties originally experienced by beginners in the manipulation of films.

The use of bromide emulsion paper for printing purposes is dealt with under *Silver printing*.

Silver Printing.

Printing on paper with silver salts may be arranged under the following three sections:—

(1) Printing on sensitised albumen paper;

(2) Printing in sunlight with gelatino chloride emulsion paper (printing out paper);

(3) Printing in artificial light with gelatin bromide emulsion, and afterwards developing.

The paper coated with albumen or gelatin is first treated with a solution of some soluble chloride, such as ammonium chloride, so that when brought in contact with a solution of silver nitrate its surface may be sensitised with the mixture of silver chloride and free silver nitrate. In the action of the light through the negative upon the sensitive paper a gradual darkening takes place during the decomposition of the chloride and albuminate of silver, and a copy or positive of the negative is produced, the lights and shades of the original object being truly represented. In ordinary silver printing the action of the light is allowed to proceed to such a length as to produce an image slightly darker than the print required, as the operations of toning and fixing have a tendency to weaken the colour of the print. At the present time albumenised paper has largely been replaced by papers coated with gelatin-chloride emulsions sold by makers as printing out papers (P.O.P.). As albumenised paper, however, is still employed in certain cases, and as the method of further treatment with it and with P.O.P. papers is very similar, a short description is given of its preparation.

As the colour resulting from the immediate action of a fixing agent on the silver compounds is a disagreeable red, the print undergoes the process of toning, which is effected by immersing it in a solution of gold, containing some substance capable of absorbing the chlorine derived from the decomposition of the silver subchloride produced by the action of the light. After sufficient tone of a brown or purple kind has been imparted to the print, the unacted-on silver compound is removed by sodium thiosulphate in the same way as with the wet plate.

To prepare albumenised paper, coat with the following:—

Albumen (white of egg) .	10 oz.
Ammonium chloride . .	100 grs.
Spirits of wine . . .	½ oz.
Water	3 oz.

Dissolve the chloride in the water and spirits of wine, then add the white of egg solution, with constant shaking for about half an hour, or, better still, break up the cellular membrane by mechanical stirring. Filter through a sponge or glass wool into a flat dish.

For plain salted paper the following quantities may be taken:—

	a	*b*
Ammonium chloride .	30 grs.	50 grs.
Sodium chloride . .	15 grs.	
Sodium citrate . .	50 grs.	
Gelatin . . .	5 grs.	5 grs.
Distilled water . .	5 oz.	5 oz.

Dissolve the gelatin in the water, then add the other substances, and filter.

To coat the paper the sheet must be held carefully by two corners, gently bent back, and the middle of the convex side of the sheet lowered on to the solution in the dish. After 2 to 3 minutes raise, and again lower, to avoid air bubbles. Float on the solution for 2 to 5 minutes, then hang up to dry.

To sensitise the paper. A silver solution, stronger than that used for sensitising the plate must generally be employed. The following give varying strengths for different circumstances :—

	a	*b*	*c*
Silver nitrate .	50 grs.	80 grs.	30 grs.
Water (distilled)	1 oz.	1 oz.	1 oz.

a may be used for ordinary cases, *b* where the negative is weak, and *c* where the lights and shades on the negative show great contrast. The strength of the bath becomes gradually lowered, and must be restored from time to time. Only strong negatives should be printed in direct sunlight ; all other cases should be exposed only to diffused daylight or covered with tissue paper or ground glass during printing.

Toning. To obviate the red colour of the printed image, it is immersed in a neutral solution of gold containing certain metallic salts. The following are some selected toning baths :—

——	*a*	*b*	*c*	*d*	*e*
Gold chloride .	1 gr.	1 gr.	1 gr.	1 gr.	1 gr.
Sodium acetate .	30 grs.	—	—	—	—
„ phosphate	—	20 grs.	—	—	—
„ bicarbonate	—	—	30 grs.	—	—
„ biborate (borax)	—	—	—	20 grs.	—
„ tungstate	—	—	—	—	20 grs.
Water . .	10 ozs.	10 ozs.	10 ozs.	10 ozs.	10 ozs.

a is a good bath for ordinary use, giving purple-brown tones, but should be made up 12 hours before use ; *b*, *c*, and *d* can be used shortly after making, and give purple tones, but do not keep well ; *e* gives fine purple-brown tones, and keeps fairly well in the dark. These solutions may also be made up in strong solutions by dissolving the tube of 15 grs. of gold in 15 oz. of water, and adding the proper quantity of alkaline salt. To make the bath for immediate use mix 1 part of the stock solution with 10 oz. of water.

The chemical reactions taking place in the process of toning do not appear to be complex in their nature, the tone being produced by a fine film of gold, reduced from a neutral solution of gold chloride ($AuCl_3$), or of the double salt ($NaAuCl_4$, $2H_2O$), upon the film containing the reduced products from the silver chloride and albuminate. To obtain the best results the gold solution must be neutral or very slightly alkaline.

Fixing the print. This is done by immersing the print, after toning, in a solution of sodium thiosulphate, 4 oz. in 20 oz. of water. This strength is suitable for prints from strong negatives, but where the print is weak the fixing bath may be reduced to 3 or 2 oz. of thiosulphate to the pint of water. Before fixing, the prints should be immersed in water containing a small quantity of sodium carbonate for 10 minutes, and then placed face downwards in the fixing bath. Their brilliancy will at first diminish, but will to a certain extent be restored when they are finally fixed and dried. The prints should remain in the fixing bath from 10 to 15 minutes, being gently moved about to prevent them sticking together. The prints must be washed after fixing for at least 24 hours in different changes of water, or for 6 in running water.

In silver printing the toning bath should be neutral or slightly alkaline, and not below 60°F. The prints must be printed rather darker than finally required, and toned to a chestnut brown, or purple.

Printing with gelatino-chloride emulsions. More rapid printing may be effected by the use of a chloride emulsion on paper, as the copy may either be printed to the full extent in a bright light, or the image if imperfectly printed may be fully developed as in the case of a plate or film transparency. The following gelatino-chloride emulsions will be found useful for such papers.

Gelatin . . .	340 grs.	Nelson's No. 1	87 grs.
		Coignet's .	87 „
Ammonium chloride	11 „	. . .	18 „
Alum . . .	15 „		
Rochelle salt . .	15 „	. . .	50 „
Water . . .	6¼ oz.		
Silver nitrate . .	115 „	. . .	75 „
Citric acid . .	62 „		
Alcohol . . .	. .	. . .	4 drs.
Water . . .	1 oz.	. . .	5 oz.

Rapid printing with gelatino-bromide paper. Paper coated with gelatino-bromide emulsion is also largely used for printing by artificial light and for purposes of enlarging. The materials and details for coating are much the same as described for the manufacture of plates or films on celluloid.

The exposures may be made by artificial light. After exposure the prints may under general conditions be developed, if necessary, intensified, or reduced, and finally fixed by the solutions already mentioned for bromide plates or films. If desired they may be toned by the gold or platinum solutions already given under *Toning* formulæ, and other colours may be given to them by the use of certain salts. Thus dark brown to red tones may be obtained by using copper salts ; green tones by mixed vanadium and iron salts ; and blue tones by iron salts. For the development and subsequent treatment it is best to use the special formulæ generally issued by the makers with the different varieties of papers. Should a combined toning and fixing bath be not used, the prints, after toning, must be fixed in the usual way.

The tone of these prints is distinctly neutral and somewhat like platinum prints. The print may be obtained dull by allowing it to dry on blotting paper after final washing, with the sensitised side upwards, or it may be obtained with a glossy appearance by being 'squeegeed,' face downwards, on a glass or ferrotype plate and allowed to dry in that position. When dry, it may be stripped from off the plate.

The printing, like that with albumenised paper, should be carried slightly further than the shade finally required, as the prints diminish in intensity during toning and fixing with certain baths.

Some Toning Baths for Gelatino-chloride and Bromide Papers.

—	*a*	*b*	*c*	*d*	*e*
Gold chloride	2½ grs.	2½ grs.	5 grs.	—	3½ grs.
Potassium chloroplatinate .	—	—	—	4 grs.	—
Citric acid .	—	—	—	45 grs.	70 grs.
Borax . .	90 grs.	—	—	—	—
Sodium acetate	90 grs.	—	360 grs.	—	—
Ammonium thiocyanate	—	90 grs.	35 grs.	—	240 grs.
Alum . . .	—	—	—	—	70 grs.
Lead nitrate .	—	—	—	—	90 grs.
Lead acetate .	—	—	—	—	90 grs.
Sodium thiosulphate. .	—	—	—	—	5 oz.
Water . .	20 oz.	20 oz.	20 oz.	20 oz.	20 oz.

(*c*) should be made up some time before using, and, if sodium tungstate instead of acetate be used, gives rich chestnut tones. (*e*) is a combined toning and fixing bath.

The toning must be carried further than in ordinary printing, and the prints may be fixed with thiosulphate directly after toning, without any intermediate soaking in water. In all silver printing processes care should be taken to thoroughly remove the last traces of the fixing agent, and the prints should invariably be thoroughly washed before drying and final mounting.

PRINTING IN PLATINUM.

Platinotype. This method of printing was introduced by Mr. Willis. It may be divided into three distinct processes. In the first the paper is sensitised with a mixture of ferric oxalate and the platinum salt, and, after exposure, is developed with a hot solution of potassium oxalate. In the second there is no platinum salt on the paper, but it is coated with ferric oxalate containing a small quantity of mercuric chloride, and, after exposure, is developed by a cold solution of potassium oxalate with the platinum salt. The third process differs from the first two in containing both the sensitive material and the developer on the paper during the operation of printing. It is, therefore, like silver printing, a printing-out process, where the image is carried to its full printing density during its exposure to the light, the print requiring no further development after exposure, but merely fixing.

In these processes the action of the light effects the reduction of the ferric to ferrous oxalate $Fe_2(C_2O_4)_3 = Fe_2(C_2O_4)_2 + 2CO_2$, leaving the potassium chloroplatinate unreduced in the film. On developing the partially-formed image, however, by warm potassium oxalate the ferrous oxalate becomes dissolved out of the film, and at the moment of its solution reduces the platinum salt, thus increasing the image by a deposit of metallic platinum

$$3K_2PtCl_4 + 6FeC_2O_4 = 3Pt + 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl.$$

Printing with hot developer. In this case the paper is coated with a mixture of ferric oxalate and potassium platinous chloride. As there is an intimate mixture of the reduced iron salt with the platinum salt on the surface of the print, when this is floated on a warm solution of potassium oxalate the ferrous salt at once undergoes solution, but in passing into solution it reduces the platinum salt, and a deposit of metallic platinum is formed, varying with the amount of ferric oxalate reduced, which differs according to the amount of action of the light on the different parts of the plate. On the high lights the ferric oxalate remains unchanged, and therefore no reduction of platinum will take place on these during development.

The paper may be prepared by brushing it over with a saturated solution of ferric oxalate, containing 60 grs. of the platinum salt to the ounce of solution. It is necessary that the paper, after it is coated, should be kept absolutely dry: this is best effected by storing it in tin boxes with lumps of calcium chloride in a perforated chamber at one end of the tin. The amount of exposure requires perhaps greater experience than in silver printing, as allowance has to be made for the circumstance that the image on the paper before development is not sufficiently marked to guide the operator in determining the length of exposure without considerable experience. Proper exposure may be said to have been given when the shadows of the picture are distinctly seen of a drab colour.

For the further development of the image the print is floated face downwards, or drawn over a hot saturated solution of potassium oxalate in the manner previously described for albumenising paper. A solution of the proper strength may be made by dissolving 2¾ oz. of neutral potassium oxalate in 10 oz. of distilled water, which should be used in a dish of enamelled iron and kept at a temperature of 170°–180°F. When development is deemed complete, and the full detail of the picture is out, the print is transferred to a solution of hydrochloric acid, of a strength of 1 oz. hydrochloric acid to 60 oz. of water, in which it should remain 10 minutes. The print must then be thoroughly washed in at least three changes of water. Should the prints be deemed over-exposed, the temperature of the developer may be lowered.

The prevailing tone of platinum prints is grey, but different tones such as brown, red and even blue may be obtained by using toning baths containing mercuric chloride, uranium nitrate or potassium ferricyanide respectively.

Development with cold potassium oxalate. In this modification of the process the paper is first coated with a saturated solution of ferric oxalate containing about 1–1¼ grs. of mercuric chloride to the ounce of oxalate solution. After proper exposure, as before described, the print is floated on a solution of potassium oxalate containing potassium platinous chloride. Considerable latitude may be permitted in the composition of this developer, but a solution containing 50 grains potassium oxalate to the ounce of water, with about 9–10 grains of the platinum salt, may be taken as a standard quantity to begin with. Warm tones are produced by lessening the quantity of potassium oxalate; cold or grey tones by increasing it.

The development by this method proceeds slowly, and may be stopped at any moment, great latitude being at the same time permitted. When the print is thoroughly soaked with the developer, it may be placed on a sheet of glass, or held in the hand, and the development watched.

Direct platinum printing without development. In this process the paper is sensitised with a mixture of the platinum salt with sodio-ferric oxalate and sodium oxalate; small quantities of potassium chlorate and mercuric chloride being also introduced under certain circumstances. This method differs from the other two in that the paper contains the sensitive salt and developer upon it during exposure, the printing of the image being carried to its full extent. Under the influence of light and the moisture in the air, reduction of the platinum salt takes place in the printing-frame. The printing must be continued until the picture has the appearance finally required. In moist weather the printing will go on without difficulty; in very dry weather the increase of density apparently stops after a certain intensity has been reached; it will continue, however, to print, if the back of the paper be breathed upon or very gently steamed.

Fixing the prints. This is best done by placing the prints in 1 vol. hydrochloric acid and 60–80 vols. water till the high lights appear perfectly white. They should then be washed in several changes of water. The tone given by platinum prints is especially applicable for copying buildings and machinery, but also yields most beautiful effects in portraiture when the proper lighting of the original negative has been attended to.

PRINTING WITH IRON SALTS.

Several processes have been brought forward in which the salts of iron may be employed instead of those of silver and platinum, thus rendering the cost of copying large plans or drawings much less expensive.

The reduction of the ferric salts by light was first utilised by Sir John Herschel, who employed ferric ammonium citrate as his sensitive material, developing the image with a solution of potassium ferricyanide, and the different methods now employed are more or less modifications of his original process.

By mixing the ferric salt and potassium ferricyanide together before coating the paper, the print may after exposure be developed by merely washing in water until the washings are colourless. For such a paper the following mixture will be found useful:—

I.	Potassium ferricyanide	200 grs.
	Distilled water	5 oz.
II.	Ferric ammonium citrate	600 grs.
	Distilled water	5 oz.

Dissolve the salts separately, then mix, keep the solution in the dark, and filter before use. The paper, after coating and drying, must be kept for a few days before use. When thoroughly exposed the print should show a bronze colour in the shadows and is developed by soaking in one or two changes of water. The colour of the prints may be improved by soaking after development in a solution of 2½ p.c. alum and 3 p.c. oxalic acid.

A method for obtaining positive prints from positives may be carried out by sensitising the paper with the following solution:—

I.	Gum arabic	4 oz.	Mix 8 vols. of II. then 5 vols. of III. to 20 vols. of I. in small portions with constant stirring.
	Water	20 ,,	
II.	Ferric ammonium citrate	10 ,,	
	Water	20 ,,	
III.	Ferric chloride	10 ,,	
	Water	20 ,,	

The paper, having been coated, dried, and exposed in the ordinary manner, may be developed by floating it on a solution of 1 oz. potassium ferrocyanide in 10 oz. of water. After development immerse in a 1 p.c. cleansing solution of hydrochloric acid or 1 : 25 sulphuric acid (sp.gr. 1·98), wash thoroughly, and dry. These methods are extremely useful for copying large line drawings or diagrams, but may also be used for ordinary landscape and portrait prints.

In the Kallitype process the paper may be sensitised by a mixture containing 75 grs. of ferric oxalate with 30 grs. silver nitrate to 1 oz. of water. The ferric oxalate is dissolved in the hot water with a grain or two of oxalic acid to assist solution. After filtering the silver is added and the solution kept in the dark.

The following may be taken as developers for this paper:—

—	*a*	*b*	*c*
Borax	2 oz.	½ oz.	—
Rochelle salt	1½ oz.	2 oz.	1 oz.
Potassium dichromate (1 p.c. solution)	15–18 drs.	15–18 drs.	8–10 drs.
Water	20 oz.	20 oz.	20 oz.

(*a*) yields black, (*b*) purple, and (*c*) sepia tones. The prints are fixed in a solution of sodium thiosulphate in 20 oz. of water to which 120 min. of ammonia (0·880) has been added.

Numerous papers for printing from negatives by silver, platinum, or other metallic salts can now be used. The formulæ and details necessary for working the individual processes are best obtained from the directions issued by the various makers.

DIAZOTYPE.

Under this heading may be classed two processes for printing in colours which may be shortly described in an article on photography. The one devised in Germany is termed *Feer-type* (from the inventor); the other is the *Primuline process*, introduced in England by Messrs. Green, Cross, & Bevan.

In the *Feer-type* the material is sensitised with a mixture of a diazo compound with a phenol or amine in molecular proportions, dried in the dark and exposed behind a negative. The azo colouring matter is produced in quantities proportional to the amount of light passing through the negative. After printing, the material is dipped in very dilute hydrochloric acid, and finally washed with water. The following table gives instances of some of the mixtures employed:—

—	I.	II.	III.
	Parts	Parts	Parts
Sodium toluenediazo-sulphonate	25	—	—
Sodium ditolyl-tetrazo-sulphonate	—	25	25
β-naphthol	25	—	—
m-Phenylenediamine	—	20	—
Resorcinol	—	—	12
Sodium hydroxide	8	—	16
Water	1000	1000	1000

Primuline process.—If primuline be treated with nitrous acid (dil.), it yields diazo-primuline, which forms various colours by combination with different phenols and amines. If, therefore, a surface be dyed with primuline, converted into diazo-primuline, and exposed to light under a negative or pattern, and be then treated with a phenol or amine, an image is obtained, the colour of which is determined by the nature of the developer used.

The material may be dyed in a hot solution of primuline, washed and converted into the diazo compound by a solution of 0·25 p.c. of acidified sodium nitrite. It is again washed, and allowed to dry in the dark. The exposure is regulated by exposing slips of the material during printing, and is known to be complete when the strip shows no colour on being touched with a drop of the developer to be used.

The development is carried out by an alkaline solution of a phenol or an acid solution of an amine (0·25 p.c.). The colours afforded by the various developers are given below:

Alkaline solution of β-naphthol .	Red.
,, ,, β-naphthol-di-sulphonic acid	Maroon.
,, ,, phenol . .	Yellow.
,, ,, resorcinol . .	Orange.
,, (slightly) pyrogallol . .	Brown.
α-Naphthylamine hydrochloride .	Purple.
Slightly acid solution of eikonogen .	Blue-black.

REPRODUCTION OF NATURAL COLOURS.

The problem of reproducing colours as they may be seen on the focussing screen of a photographic camera has long attracted the attention of those engaged in experimental work connected with photography. It is, however, only in recent years that processes founded to a considerable extent on the work of early experimenters have yielded satisfactory results.

This branch of photographic practice has developed so greatly within the last few years that any account of it in a work of this kind must of necessity be brief and somewhat general in its nature, and special works must be consulted for specific details connected with the various processes.

The methods employed for the production of coloured effects on sensitive films may be divided into two large classes. (*a*) Those where the result is produced by the direct action of light on the sensitive material; and (*b*) those produced by the intervention of coloured screens, either separate or combined with the sensitive film.

In (*a*) the colours are reproduced (1) by direct action on the sensitive material, (2) by interference of the waves of light reflected back through the film from a mirror, and (3) by the bleaching out of certain dyes which are responsive to the action of the various coloured rays. In (*b*) the effects are produced either by coloured screens of various patterns superimposed on the sensitive material or by grains coloured in blue, green, and red, and incorporated in the sensitive film itself.

Becquerel and Niepce. That a sensitive silver film by itself could respond to coloured rays of light was observed at an early date, and about 1810 the German physicist, Seebeck, showed that different gradations of colour effect might be obtained when the solar spectrum was thrown on a film composed of moist silver chloride. Such changes of colour on silver salts were also noticed by John Herschel, Hunt, Fox Talbot, and others; but at that time little progress was made until the experiments of Becquerel and Niepce between 1850 and 1855. In all of them, however, the long exposure necessary to obtain an effect, the very moderate reproduction of the colour effect, and the impossibility of permanently fixing the picture, rendered all such attempts impossible for producing results with the camera.

Lippmann's method by interference waves. This process, in which no coloured materials or screens are employed, depends upon the production of the colour phenomenon by the interference of light rays reflected from thin films. The plate coated with a transparent emulsion and impregnated with colour sensitising media is placed in a special dark slide with the glass of the coated plate facing towards the lens, and the sensitive film in close juxtaposition to a thin bath of metallic mercury, which acts as a reflecting surface.

The light rays passing through the film are reflected back from the surface of the mercury, thus producing a number of stationary periods or nodes due to the neutralisation of the opposing incident and reflected rays.

The circumstances which produce this effect in the plate may be shown by a diagram (Fig. 8), illustrating the movement of rays of different velocities through a thickness of the sensitive material.

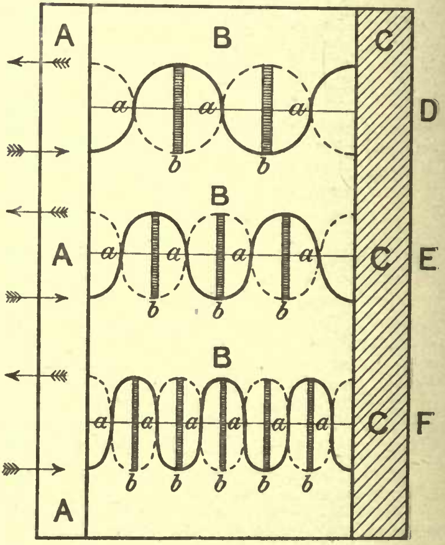


FIG. 8.

In this diagram the rays of the red, green, and blue colours, indicated respectively by the letters D, E, and F, passing through the film and falling on the mercury C, are indicated by the continuous lines, while the dotted lines represent the reflected rays. At the points *a*, *a*, *a*, the rays intersect each other, giving no movement at these points, and, consequently, no light effect, whereas at the points *b*, *b*, *b*, or internodal points as they are called, where no interference exists, the action of light will cause a deposition of silver. This deposition taking place at a separation of half a wave length of the incident, light will only reflect light of the colour, the wave length of which is double the distance of these internodal points.

Originally Lippmann employed an albumen process for his sensitive plates, colour-sensitised with erythrosin, quinoline red, cyanine, and malachite green; but more recently formulæ for gelatin emulsion plates have been put forward by Valenta, Lumière, and by Lippmann himself. The following numbers give two forms of the emulsions that have been proposed :—

		I.	II.
A.	Gelatin . . .	10 grs.	5 grs.
	Silver nitrate . .	6 grs.	3 grs.
	Water . . .	300 c.c.	225 c.c.
B.	Gelatin . . .	20 grs.	5 grs.
	Potassium bromide .	5 grs.	2·1 grs.
	Water . . .	300 c.c.	225 c.c.

For colour sensitising cyanine and erythrosin solutions (1 : 500) have been used. For the sensitiser 2 parts of the cyanine solution is mixed with 1 part of the erythrosin solution, and 1 to 2 parts of this mixture added to 100 parts of the emulsion. Increased sensitiveness may be given to these plates by bathing them shortly before exposure in a mixture of 5 grams of silver nitrate dissolved in 1000 c.c. of alcohol, to which 5 c.c. of acetic acid have been added.

Ives' process. This process, devised by Ives in America and by Ducos du Hauron in France, depends on the principle put forward by Clerk Maxwell, that the object to be reproduced, if photographed through three separate coloured screens, will give corresponding negatives representing in light and shade the gradation to which the different light effects coming from the object will excite a single primary colour sensation in the eye. Three negatives of the object are obtained, one taken behind an orange screen, a second behind a green, and a third behind a blue screen. Three positives are then taken from these negatives, and are illuminated one by red, the second by green, and the third by blue violet light. These being superimposed on a screen, the combined image of the original object will be seen reproduced in its natural colours.

For the simultaneous production of the negatives and for the projection on the screen, special cameras have been devised, and for viewing the transparencies Ives introduced the apparatus known under the name of the 'Kromoscope.'

The same effect may be obtained on one glass plate in the following way. Three separate negatives are taken, paying due attention to the exposures necessary for the different coloured filters. These are developed in the usual way, fixed and washed. To obtain positives from these negatives, an ordinary transparency is first taken from the negative obtained through the red screen, washed and dried. It is then bleached by immersion for about a minute in a solution of potassium ferricyanide, washed with water, and placed for a minute and a half in the red staining solution. The stained film is then transferred to a solution of sodium thiosulphate, which at first causes a brown precipitate. This is at once thrown off and fresh thiosulphate flowed over the plate, when the image will gradually assume a greenish-blue colour. The plate is now washed, dried, varnished with a celluloid enamel, and again dried.

The pink and yellow images may then be printed at the same time on one strip of a sensitised dichromated gelatin film, the celluloid side of the film, not the dichromated side, being in contact with the film side of the negative, so that the print is made through the celluloid support. The film is then developed in the usual manner by hot water at a temperature of 95°–100°F., fixed by sodium thiosulphate, and thoroughly washed with cold water. The two prints are now cut separate and stained by the pink and the yellow dyes. The staining should be carried out in white porcelain dishes, and should be done slowly.

When the stained transfers have been rinsed and dried they are ready to be superimposed in correct position over the blue transparency first described. The pink film is first accurately adjusted film to film over the blue, and then the yellow, stained side downwards, over the pink. The films may be fixed in accurate register with binding slips, but a better result is obtained if the separate films are secured in optical contact by Canada balsam. When thrown on the screen the original picture is reproduced.

Dyes for tri-colour staining. The following are some of the substances which may be used. For blue: thio blue A or soluble Prussian blue, slightly acidified with sulphuric acid. For pink: a mixture of eosin and rhodamin pink. For yellow: best brilliant yellow or aniline yellow. For Ives' plates. For blue: methylene blue, 16 grs.; cold water, 4 oz. For pink: magenta red, 16 grs.; hot water, 4 oz.; acetic acid, 10 mins. For yellow, ammonium picrate, a saturated solution. In each case the transfer, after staining, should be rinsed in water slightly acidified with acetic acid.

The nature of these dyes is very varied, and special works must be consulted with regard to quantities and methods of preparation.

Light filters for colour work. These may be made with either a collodion or a gelatin medium coated on glass or used in cells. For yellow light filters: tetrazine, rapid filter yellow K; aurantia, and naphthol yellow may be used. For orange filter a mixture of aurantia or rose Bengal with tetrazine is employed.

Filters for three-colour work. For these a 6 p.c. stock gelatino solution is the medium. For the violet filter (yellow printing negative), stock dye solution, crystal violet, 31 grs.; warm water, 6 oz., 76 mm.; glacial acetic acid 3 mm. Add 20 parts dye solution to 100 parts gelatin solution. A second blue dye is rapid filter blue, 15¼ grs.; water, 6 oz., 160 mm.; ammonia, 10 mm. Filter, then take dye solution 20 parts; gelatin, 100 parts. For green filter (red printing negative). Rapid filter green I., 62 grains; water 3½ oz. Take of dye solution 20 parts to 100 of gelatin solution. A green for panchromatic plates is as follows: filter blue-green, 15¼ grs.; filter yellow K, 15¼ grs.; water 3½ oz.; take dye solution, 20 parts; gelatin, 100 parts. Red filter (blue printing negative). Rapid filter red I., 38½ grs.; water, 3½ oz. Take dye solution 20 parts, gelatin 100 parts.

Single plate coloured processes. Joly's process. In this process a glass screen, which may be called for convenience the taking screen, is ruled mechanically with minute lines in orange, yellowish-green, and blue. This screen is placed in the ordinary camera slide with the lined surface inwards and in contact with the film of the sensitive plate. These plates must be sensitive to the entire range of colours. The negative having been developed in the usual way a positive is printed from it by contact, and another ruled screen is placed in contact with this transparency. This second screen, which may be called the viewing screen, is not lined like the first one, but in red, green, and violet lines. This screen must be so adjusted that the red lines fall on the position originally occupied by the orange lines of the taking screen; the green on that occupied by the blue-green, and the violet on that originally occupied by the blue. It is of importance that the lines be in exact register. The positive and screen having now been put in exact position, the image can be thrown upon a screen, when the picture will be seen in its original colours. It is of advantage that these pictures should be looked at from some little distance, as the lines blend more harmoniously, and they should also be looked at directly, as when seen obliquely the colours vary. When observed directly the lines on the positive, and those on the viewing screen are in register; but when observed obliquely, the blue or red predominate, according to the side from which the transparency may be regarded.

Autochrome process. In this process, introduced by Lumière, the colour screen consists of minute starch granules dyed with the three primary colours, red, blue, and green, this film being overlaid by a panchromatic sensitive film. In preparing these the plates are first coated with a tacky film which is then covered with a layer of the coloured granules thoroughly mixed, so that the different colours may be as far as possible uniformly distributed over the plate. This film is then rolled so as to get it as thin as possible, and retaining on its surface only one single thickness of the coloured particles. It is then dusted with some black material to fill up the interstices between the coloured granules, and finally dried and varnished. In some cases the dark material is incorporated in the emulsion containing the coloured granules. Upon the plate so prepared is spread the panchromatic sensitive emulsion, which is dried in the usual manner and it is then ready for use.

The plate, as in the case of all such in which the coloured screen is attached to the sensitive film, must be exposed with the glass and not the emulsion towards the lens, so that the light coming to the sensitive film must pass through the coloured filter. The lens must also be covered with a yellow screen to diminish the active effect of the violet-blue rays.

This reversal of the position of the plate in the camera necessitates some adjustment of the focus in using an ordinary carrier and ground glass focussing screen. Such compensation can be made either by reversing the ground-glass screen or by racking in the lens about $\frac{1}{16}$ of an inch towards the plate, thus compensating for the depth of the glass plate on which the emulsion is spread. It may also be arranged for in more simple manner by focussing the image on the ground glass before placing the yellow screen in its position behind the lens. On screwing the yellow screen into its proper position, after focussing in the ordinary way on the screen, the image will be found perfectly sharply reproduced on the developed plate after exposure.

Dufay's dioptichrome process plate. In this the colour screen consists of a series of parallel green lines with the intervening spaces filled by alternate blue and red squares. The breadth of the lines and the size of the squares have a certain relation; thus the width of the green line is 0·06 mm.; the blue square is 0·06 mm., and the red square 0·07 mm. The plates are rapid and are said to be stronger for handling than some of the others.

Thames screen plate. This plate has a colour screen formed of rows of alternate red and green circular disks, the intervening spaces being filled with a violet-blue dye, thus covering the entire plate with the three colours. The Thames plate can also be obtained with the colour screen separate from the sensitive plate.

In these plates the screens are apparently more transparent than when coloured granules are used; also they can be exposed with a lighter yellow screen upon the lens and probably are more rapid in their action.

Development of coloured positives. Unless it be necessary that the resulting positive should undergo intensification, the development may be carried out with only two solutions, the developer and the reversing solution. The same reducing agents, with some slight modifications, may be employed as are used in the ordinary developing solutions already described. The most important differences from the ordinary manipulation in the development of coloured positives are that the light of the developing room must be much more modified on account of the sensitive nature of the plates, and the washing operations as short as possible on account of the delicate nature of the films.

The first development is carried out in the usual way, but should be finished in 2 to 2½ minutes; the plate is then carefully washed and covered with the reversing agent, an acid solution of potassium permanganate or dichromate. At this stage it can be taken into daylight and examined. The plate may be allowed to remain in the reversing solution for 3 to 4 minutes, but must be closely watched. It is then again washed and flooded with the same developer as employed in the first development. Both the reversal and the second development may be carried out in daylight and the action of the second development allowed to proceed until the positive becomes uniformly dark or nearly black when viewed in the dish by reflected light. Should the positive appear dull or slightly stained after reversal it may be cleaned by immersion in a 1 p.c. solution of sodium meta-bisulphite. Full instructions are generally given by the makers of the various plates.

The following may be taken as more or less applicable to plates where the colour screen is combined with the emulsion.

Developers.

	a	*b*1
Metaquinone (quinomet)	½ oz.	—
Sodium sulphite (anhydride)	3½ oz.	—
Potassium bromide . .	90 grs.	60 grs.
Ammonia (0·920) . .	9 drs.	—
Hydroquinone		½ oz.
Potassium metabisulphite . . .		½ oz.
Water	35 oz.	20 oz.

	*b*2
Caustic potash	1 oz.
Water	20 oz.

a is the developer generally applicable to autochrome plates and *b*1 and *b*2 to Thames plates. In these latter, *b*1 and *b*2 should be mixed in equal quantities just before use.

Reversal.

—	*c*	*d*	*e*
Potassium permanganate	30 grs.	—	—
,, dichromate .	—	45 grs.	10 p.c. solution 1 oz.
Sulphuric acid . .	35 drs.	100 mm.	1 dr.
Water . . .	35 oz.	20 oz.	10 oz.

c and *d* are useful for autochromes, *e* is generally used with the developers *b*1 and *b*2 for Thames plates. In using potassium permanganate as the reversing agent it is often necessary to immerse the plate for a few seconds in a bath of chrome alum immediately after reversal and before the final washing.

Intensification. Should the plate after development appear to want contrast and brilliancy it may be intensified either at the time of development or at some future time provided it has not been varnished. Before intensification if the plate has been allowed to dry a thin edging of varnish should be given to it to prevent the film frilling or slipping.

The plate is first immersed for about 15 seconds in a solution of—

Acid permanganate from developer (*c*)	5 drms.
Water	35 oz.

After washing it is intensified much in the same manner as described for wet plate positives in the following solutions:—

I.	Pyrogallol . . .	45 grs.
	Citric acid . . .	45 grs.
	Water	35 oz.
II.	Silver nitrate . . .	75 grs.
	Water	3½ oz.

Of these for any size up to a whole plate take of I. 3½ oz. and of II. 3 drms.

Immerse the plate in this solution and examine the increase in intensity from time to time. The solution must be made just before use and discarded when it becomes turbid. After intensification, gently wash the plate for a few seconds and immerse in a bath of *neutral* permanganate containing potassium permanganate 15 grs. to water 35 oz. Wash again for a few seconds and fix the plate in the following bath: sodium thiosulphate, 5½ oz.; saturated solution of sodium bisulphite, 1¼ oz.; water, 35 oz. The plate after a final washing can then be dried. Fixing the plate in thiosulphate is always necessary after intensification.

Bleaching-out process. This process depends upon the fact that certain dyes may be destroyed by the rays of light which they absorb. Thus an unstable red colour will be stable in red light but be destroyed by light of another colour; this phenomenon, as explained by Herschel, being due to the fact that only those rays which are absorbed by a dye can exercise their energy in decomposing that dye, the other rays which are reflected having no action upon it. Thus if a film be constituted of properly chosen yellow, red, and blue dyes, only those dyes will be destroyed which absorb the rays of the corresponding colours. If paper be coated or otherwise dyed with sensitive aniline colours which are especially susceptible to this decomposition and a coloured transparency be placed upon it, wherever green light falls upon the paper the red and blue colours will bleach out, and conversely where red falls the blue and green will bleach, and where blue rays fall the red and green will go. In fact, wherever a particular colour falls, that special colour will be retained and rendered permanent on the paper print.

The following quantities have been given as suitable for preparing a sensitive film for this process:—

A.	Gelatin	154 grs.
	Distilled water . . .	3½ oz.
(1)	Methylene blue . . .	1½ grs.
	Distilled water . . .	1¾ oz.
(2)	Auramine	1½ grs.
	Alcohol	1¾ oz.
(3)	Erythrosin . . .	4 grs.
	Distilled water . . .	1¾ oz.

To the gelatin solution A add of No. 1 solution 68 min., and of No. 2, 34 min., stir well and then add drop by drop with constant stirring 25 min. of No. 3 solution. The addition of No. 3 must be stopped on the slightest appearance of a red tinge. The mixture should stand for 3 or 4 hours at a temperature of from 95° to 110°F., and then should be added a solution of chloral hydrate 31 grs. and caustic soda solution 30 p.c., about 10 min.

The length of exposure necessary to give any good result is at present so long, that this method of obtaining coloured prints cannot be said to be quite perfect enough for ordinary use. Improvements, however, are being made. It will be seen that this process, if the films be spread on paper, might be used for printing from coloured transparencies.

PRINTING IN COLOURS ON PAPER.

In the processes hitherto described the result obtained is a coloured transparency on glass of which only one copy can be retained. To obtain a number of copies on paper, resort must be had to photo-mechanical work. The principles involved in these processes will be dealt with elsewhere (p. 236), so that here it is only necessary to describe the differences which exist when producing such pictures from coloured transparencies.

Three negatives of the subject are first taken through proper colour filters as already described, and from these, corresponding positives are made on ordinary sensitised plates. Cross-hatched negatives are now made from these positives through lined or dotted screens as for ordinary photo-mechanical printing, which negatives can be printed on copper or zinc plates coated with dichromated gelatin. Development by washing is then carried out in the usual way, leaving a positive in insoluble gelatin on the copper or zinc plate. These constitute the three blocks, as they are called, and may now be coloured separately in yellow, red, and blue, the final prints being taken from them by carefully superimposing and adjusting the sheet on which the final impression is to be taken. The order in which the final printing is carried out is first to print the yellow image then the red and finally the blue.

Collotype colour process. The final prints in this process are obtained in the various colours from a reticulated gelatin surface. Three negatives are taken in the manner already described on thick glass plates covered with dichromated gelatin, and after exposure washed to remove the colour of the dichromate. When dry the plates are soaked in glycerol and water for about 30 minutes, and the solution carefully removed by a dry cloth. The glycerol solution penetrates through the film, apparently according to the different intensity of the light that has acted on various parts of the plate. Thus there is great penetration in the parts unacted on by the light, but little or none on the portions hardened by the light. On covering the surface with coloured ink, the greasy body adheres to the dryer shadows, but does not become attached to the more moist portions which represent the high lights. The final impressions are taken by accurately superimposing the sheet of paper successively over the three differently coloured collotype plates. The reticulation of the gelatin in this process provides the necessary fine grain on the plate.

Imbibition process of Sanger-Shepherd. Three negatives are first taken through the colour screens, and positives printed from them on a celluloid film coated with gelatin containing silver bromide, which is sensitised in a solution of potassium dichromate. The prints are made by printing *through* the celluloid film, the celluloid surface being in contact with the film side of the negative. Exposure is carried on until all details are visible on the film as a dark yellow print. The film is now washed for some minutes in water and then fixed with sodium thiosulphate until all the white silver bromide has disappeared, leaving the image in clear gelatin. The film, taken under the green filter negative, is now stained in the pink dye bath, that from the blue filter in the yellow dye bath, and the third stained in the blue dye.

The prints are then successively 'squeegeed' on to a sheet of paper which has been coated with a thin layer of gelatin, and which after well soaking in water is spread on a glass plate. The order in which the dyed positives are transferred to this coated paper is, first the one dyed in the pink colour, second the yellow dyed positive, and finally the one with the blue dye. By this means a combined print formed from the three combined colours is obtained.

Pinatype process. This process depends upon the use of certain dyes which do not attach themselves to the hardened gelatin, but are capable of staining the unacted on gelatin. This is the reverse of the last described process, and as the dyes do not attach themselves to the hard, but only to the soft gelatin, the print in this case will be a facsimile of the original negative. In order, therefore, to make a positive print, the dichromated plate must be made from a transparency and not from a negative.

Three negatives having been taken through coloured screens, three positives are copied from them on an ordinary emulsion, similar to that used for lantern slides. From these positives, three sensitised dichromated printing plates are made, which after washing and allowing to dry are dyed with blue, red, and green pinatype dyes; a blue bath for the plate made from the red screen negative, a red bath for the plate from the green screen negative, and a yellow bath for the third plate.

To print the picture on the transfer paper, which has been previously well soaked in water, it is gently 'squeegeed' first on to the blue dyed plate, then on to the red and finally on to the yellow. It is not absolutely necessary to follow this order, as it has been found advantageous to alter it for different subjects. About 10 minutes will suffice for the transfer of each colour to the transfer paper, but for details with regard to this and for the minute manipulation of the process, special instructions must be consulted. It will be observed that a certain advantage exists in this process, as the three colour impressions are obtained on the one gelatin support.

Two-colour process. A process employing only two colours has been introduced by Gurtner of Berne. In this exposures are made of the blue and yellow negatives, but no attention is paid to the red. A chloro-bromide transparency plate is first dyed in the dark for a few minutes in an aqueous solution of naphthol orange and then dried. This plate is now placed film to film in contact with an ordinary panchromatic plate in the dark slide, so that the glass of the former, or transparency plate, faces the lens. With this arrangement the orange dyed plate acts not only as the senstive plate for the blue rays, but also as a light filter for the red, yellow, and green rays. In this way, the transparency plate becomes the negative for the yellow print, and the panchromatic plate that for the blue print.

From the panchromatic plate, a blue print is made by printing in ferro-prussiate paper or some other known method. The transparency or yellow plate, after fixing and washing away the stain, may be printed from on ordinary printing out paper, or on a stripping collodio-chloride paper, and if the prints be fixed with ammonia without toning they will retain a proper yellow-red tone. If transparencies are used the yellow transparency is directly combined with the blue by placing the plates film to film. If prints on paper are required, then the print on the stripping collodio-chloride film after careful adjustment is superimposed on the blue print. J. M. T.

PHOTO-MECHANICAL PROCESSES.

In addition to the processes of pure photography in which the results are obtained by light action aided by subsequent chemical operations, there are other methods of photographic picture making. These constitute a group by themselves of considerable industrial importance, differing from the purely photographic methods in so far that they yield their results partly by chemical and partly by mechanical means. Photography is utilised in the production of surfaces from which prints are afterwards obtained in printer's ink. Such processes employ the different forms of printing press, and, to them the term *photo-mechanical* is applied. They are used for the production of transcripts of drawings and paintings of different kinds and for the multiplication of copies of photographs of natural objects. By far the greater portion of the illustrated books and periodicals now made utilise photography in this manner. The processes are divided into three groups, *intaglio*, *surface*, and *relief*, according to the form of the ink-bearing medium. The term 'surface' is for convenience generally employed (although it is not strictly correct), and it is the function of this photographically prepared surface to hold the ink (afterwards to be transferred to paper) distributed in such order and quantity as will render the various tones of the picture. For a simple understanding of the differences in the three groups, consider a plane surface as the starting-point. Then, in an intaglio process, the ink-holding portions are sunk below that surface, as, for example, in a steel engraving—in a *surface* process the ink-bearing parts and those which do not bear ink are in the plane of that surface after the manner of a picture upon a 'lithographic' stone, whilst in a *relief* process certain portions of the original surface have been removed, forming depressions, leaving other portions which are to bear ink standing in relief, the simplest illustration of this form of surface being an ordinary woodcut. It will be seen that a relief process—so far as the finished result is concerned—is the exact reverse of an intaglio process. Methods coming under these two designations yield printing media which fulfil their purposes by utilising purely mechanical principles. This is not so, however, with surface processes, for the physical state of the surface produced by chemical change largely determines their working.

The following list gives the typical and more important processes according to their character in the groups already given :—

Intaglio.

Photogravure in line and in gradated tones—flat surface.
Photogravure in line and in gradated tones—cylindrical surface.
Woodburytype.

Surface.

Photo-lithography.
Photo-zincography.
Alagraphy.
Collotype.

Relief.

Line block processes.
Tone ,, ,,
Colour processes (tri- and multi-colour methods).
Combination processes between methods in the same group or between those in more than one group, as for example, collotype and lithography, lithography and tone block processes, lithography and photogravure.

Negatives required for photo-mechanical methods are made by means of wet collodion, collodion emulsion, and by dry plates. The first-named process is the one principally used for the majority of purposes, for the reason that it is the most economical and gives easily the kind of negative required. When, however, subjects in colour are to be rendered either in monochrome or again in colour, the choice lies between the two latter methods. The modern orthochromatic dry plate of the best type has, however, very largely replaced collodion emulsion and will probably in time do so entirely.

The second step is the making of the surface. Practically the whole of the photo-mechanical processes are based upon the changes which occur when albumen, gelatin and its degradation product gelatose (of which the substance 'fish glue' is the most important example), are exposed to light in conjunction with alkali dichromates. Generally the insoluble bodies so produced are employed as protective agents or 'resists' upon the surface of a metal against the action of some solvent of that metal (photogravure and relief block processes), or they may be used in the production of an ink image to be applied to stone or metal as an intermediary (lithography, zincography, alagraphy), or to paper as finality (collotype).

Intaglio Processes.

Woodburytype. This process was the invention of the late W. B. Woodbury, and is especially interesting in that it forms a bridge between the purely photographic and the photomechanical process. The printing plate consists of a sheet of lead which is impressed with a series of cavities the variation in depth of which corresponds to the light and shade of the different portions of the picture it represents. A carbon print (see *Chromium Printing*, p. 241) is a picture produced in insoluble gelatin which holds in suspension finely-divided carbon or other pigmentary matter. The picture tones are represented by various thicknesses of insoluble gelatin, and such tones show a sensible amount of relief. By the use of a specially thick film of gelatin the amount of relief may be increased, and if such a film be developed upon a film of collodion there is obtained what is known as the Woodbury 'relief,' which is merely a carbon picture held upon a thin film of textureless collodion instead of upon the fibrous paper, as is customary with a carbon print. When the film is dry, there are varying thicknesses of hard gelatin, and it so happens that such is capable of resisting considerable pressure. If the relief be laid upon the bed of a hydraulic press and a sheet of pure lead be put above it and pressure applied (the precaution being taken to prevent the lead flowing laterally), a perfect mould will be made of the relief, and without damage to the gelatin picture. The gelatin relief can be readily removed and the result will be an intaglio copy in lead. If, when the carbon print has been removed, the space left is filled up with a solution of gelatin containing pigment and this gelatin is allowed to set, to all intents and purposes, the condition is the same as it was in the first instance, except that one filling material was dry gelatin, and the other is wet gelatin. If we allow this gelatin to set, attaching to it previously some substance by which it can eventually be withdrawn, a print will be produced similar to the one used for making the mould. The latter was a carbon print produced by the agency of light, and now from a leaden intaglio plate or mould a similar carbon print is obtained, purely by mechanical means and without light action. When once the leaden relief is produced, prints are readily made merely by pouring into the mould a solution of gelatin containing pigment suitably adjusted as to quantity, placing on the top a sheet of paper, and applying even pressure above. The excess of gelatin is squeezed out at once, that remaining in the mould sets in a short time, and upon lifting the paper away the gelatin will come with it. A Woodbury print is then simply a carbon print produced mechanically and consists, as does the carbon print, of a layer of gelatin of varying thickness, the only other difference being that in the case of the light-produced carbon picture the gelatin is insoluble, and in the mechanically-produced carbon print it is not. This process is probably the most perfect of all the photo-mechanical processes, so far as the rendering of tone is concerned. Very great variety can be obtained, the colour depending upon the pigment used with the gelatin. The process *Stannotype*, also due to Woodbury, was a modification of this method designed to avoid the necessity for hydraulic pressure in the production of a mould. The plate was formed from a negative carbon relief in gelatin faced with tin foil forced into contact with the relief by rubber roller pressure.

Photogravure. A photogravure plate is a sheet of copper bearing an image formed by means of cavities of different depths, which represent the gradations of the picture. These cavities are filled with an ink composed of linseed varnish and a pigment (for example, lamp black), which ink is afterwards transferred to paper by means of pressure in the copper plate printing press. The process most generally used is that known as the Talbot-Klic.

Any drawing in line or gradated tones in monochrome or colour or any photograph of a natural object may be rendered by this process. Whatever be the original, a negative must first be prepared of the desired size, and from this negative a positive transparency is made which should be laterally reversed. If the subject be a line drawing the positive may be produced by means of a gelatino-bromide dry plate or by wet collodion. If the negative represents a drawing in gradated tones—for example, a wash drawing, an ordinary water colour or an oil painting or a photograph of a natural subject—it should be unreversed and from it a positive transparency is made by the carbon process, which produces the reversal required without further operation. The method gives probably the best rendering of tone, but in the hands of a skilful operator a reversed positive may be made by the dry-plate process. The latter plan has the advantage that the size of the positive may be varied from that of the original negative which is frequently required.

Outline of process. The process of photogravure consists in forming upon the surface of a sheet of copper, on which there is deposited a fine dust of bitumen (or colophony), an insoluble gelatin image. The plate bearing the dry gelatin image is placed in a solution of ferric chloride which is absorbed, when swelling and penetration of the film takes place—the solution eventually reaches and then etches the metal. This process may be termed 'through' etching. The various thicknesses of the gelatin which form the gradations of the image determine the commencement of the action of the mordant, so that in a given time different amounts of etching are produced, corresponding to the tones of the picture. When the etching is completed the gelatin is removed, the plate cleaned, and it is then ready for proofing in the press.

This gelatin image governing the etching is a negative image, and is the 'resist.' It is produced by the carbon process, in the ordinary manner of the carbon printer, by developing on the metal a tissue exposed under the reversed positive from the negative of the subject. The dust coating is termed the 'grain.' Its function is to protect minute areas of the surface of the metal from the attack of the mordant. A patch of uniform tone of appreciable size is not represented by an etched cavity corresponding in area to that patch of tone, but is made up of a number of small ones, undistinguishable as separate elements by the unaided eye.

Failing this condition—however it may be produced—in the plate, the printing ink could not be held prior to transfer to the paper which forms the final support of the image.

The 'grain' is produced by exposing the plate in a box which contains suspended in its atmosphere very finely divided bitumen or colophony. The 'graining box' must be of considerable volume and large in horizontal sectional dimensions in proportion to the dimensions of the copper plate, in order to enable uniform graining to be obtained over the whole area of the surface. When the amount of dust deposited is sufficient the plate is removed and gently heated, when the grains soften and adhere firmly to the metal. The success of the process is largely dependent upon suitable graining of the plate.

The copper used for plate making must be pure, hard, and homogeneous, the surface planished and highly polished. The carbon tissue is preferably one containing only a small quantity of pigment in order that the colour of the metal may be seen through the film. The correct exposure for the tissue under the positive should be ascertained by trial exposure, developing such trials upon opal glass.

The solution of ferric chloride (which must not contain free hydrochloric acid) employed as mordant is prepared by dissolving the salt in water to that degree of saturation which registers 45°Baume at 16°C., and from this solution others are prepared by dilution to densities 33°, 35°, 38°, 40° and 43°B. The more concentrated the mordant the slower the rate of penetration. A very concentrated solution may not in reasonable time penetrate even the thinnest portion of the resist. If such fails, the solution is poured away and a weaker one employed. When the ferric chloride reaches the copper, a darkening takes place showing that the etching has started. Such action will continue to other and lighter tones as the mordant penetrates, and to secure this end the weaker solutions are used successively until even the thickest layer of gelatine is penetrated. Errors in timing or in the use of unsuitable solution lead to faulty rendering of the scale of gradation.

When the etching is completed the metal plate is at once placed in a solution of caustic soda, which arrests the action of the mordant. The plate is washed in water, scrubbed with a soft brush, brushed with dilute sulphuric acid, and afterwards with turpentine to remove the "grain," again washed and dried.

The plate is printed after the manner of a copper plate etching, and in photogravure much of the success is due to skilful treatment in this operation. If only a few copies are required the plate may be printed at once; but for any quantity it is necessary that the surface be 'steel faced,' in order to protect the image from wear in the printing process.

Usually photogravure plates require considerable modification at the hands of a skilful engraver by means of the burnisher and roulette, and by a process of selective etching for which the plate is afterwards specially prepared.

INVERT HALF-TONE INTAGLIO PRINTING.

A form of intaglio printing consists in adapting the ruled screen half-tone principle (see *Tone block processes*). A screen positive is made from an ordinary negative (continuous tone) and from this positive a print is made upon copper by the enameline process (see *Enameline printing*). This print forms the resist. The plate is afterwards etched in a solution of ferric chloride, and the etched metal is printed in the copper plate printing press. The gradations of light and shade are rendered by dots of various sizes (the number per unit area depending on the ruling of the screen employed when making the screen positive), as in the half-tone block process, but each etched cavity is the same depth.

ROTARY PRINTING OF INVERT HALF TONE.

Instead of using a flat surface of copper, a cylinder of the metal may be employed. This offers considerable advantages, inasmuch as it permits of the adoption of the rotary method of printing with the consequent gain in speed of output and in certain other directions the process is useful, as, for example, in the illustration of the less expensive forms of printed matter, newspapers, periodicals and the like. Special devices are used by which the sensitive coating (fish glue and an alkali dichromate) is applied to the roller and a flexible film form of half-tone screen positive is caused to adhere to the cylinder by a suitable fluid medium—as, for example, mineral oil—which does not affect the sensitive coating. After exposure to light, the image is developed, dried, and enamelled. Those portions of the roller not covered with an image are now varnished by a protecting medium and afterwards the roller is treated with the mordant. The printing of such cylinders differs from that employed with any other photomechanical process. The machine employed consists of a large cylinder or bowl upon which is stretched a felt blanket, and over this is fed the paper from an endless reel. The engraved roller is supported in contact with the printing paper, the pressure between the two being variable at will. The inking is effected by supplying the printing colour to the roller as it revolves by the aid of a brush or felt feeder. The excess of colour is removed by means of a thin steel knife-edge blade termed the 'doctor,' which is caused to press upon the roller with sufficient pressure to remove the superfluous ink from the surface. The colour remains in the etched hollows. The surface-clean portion of the roller next comes in contact with the printing paper, when transference of the colour from the cavities takes place. It will be seen that the steel 'doctor' with its perfectly smooth edge replaces the hand wiping of the copper plate printer. Perfect fitting of the two surfaces, the 'doctor' and the cylinder, is necessary. The ink used must be much thinner in consistency and of a different character to that employed for ordinary copper plate printing or the surface of the roller cannot be made clean by the 'doctor.' This method of inking does not offer the same opportunity for modification as that used by the ordinary copper plate printer, whose craft is extremely personal, offering abundant field for the exercise of taste. In consequence, excellence of result in all 'doctor' or mechanically wiped intaglio printing depends largely upon the quality of the engraving work.

ROTARY PRINTING OF PHOTOGRAVURE.

Rotary photogravure. The method of printing ordinary photogravure plates does not lend itself to speed of production, and the result is that the prints are relatively costly, especially for large sizes. Photogravure plates, as in the case of ordinary copper or steel intaglio etchings, can be printed with success upon special flat-bed printing machines, when the wiping of the plates is effected by means of a 'doctor' or by a travelling band of paper. It is, however, found in the case of the delicate photogravure plate that considerable wear takes place. For some years, the rotary principle has been applied with great success in the case of a limited number of firms, where methods of producing the etched rollers are carefully guarded secrets. The 'invert half tone' process should not be regarded as the same as photogravure, for the reason that 'through etching' is necessary to give the characteristic effect of the latter process, the etched cavities of the rotary photogravure plate, unlike 'inverted half tone,' varying in depth, an important element in producing the beautiful effects of the method. If upon the surface of a copper cylinder there be developed a carbon print made by exposing a sheet of sensitive dichromated tissue under a ruled screen (see *Half-tone process*) of special type (Fig. 12), the tints so produced—which are formed of regularly distributed elements of insoluble gelatin—may be utilised in place of the bitumen grain employed in the Talbot-Klic process. Upon this ground, a carbon negative image—as in the Talbot-Klic process—is developed and the roller with duplex resist is, when dry, submitted to the action of ferric chloride. The roller so prepared is then printed after the manner previously outlined.

The quality of result obtained by the rotary process adopted by the best firms is very high, the rollers being singularly free from obvious evidences of the use of the hand engravers' tools. This is largely due to the perfection of the method itself and to the attention paid to the making of the negative and positive and to their skilled retouching. The printing ink—the medium, pigment, and viscosity—the paper used, and the speed of printing require very careful adjustment, the one to the other, and to the particular engraving on the roller.

Photogravure in colour. Prints in colours are produced by applying colour inks to the engraved plates, which are etched more deeply than for monochrome. The coloured inks are applied to the plates by sponges or by dabbers of different sizes and for small details by stumps, and the plates are wiped by the usual muslin and also by the soft portion of the printer's hand. The transfer of the ink to the paper is completed at one operation. The process is naturally slow, and the results, though often very fine, are costly.

Recently, the rotary principle has been applied to the production of photogravure prints in colours with success. Combinations of rotary photogravure and lithography for colouring work are also employed.

CHROMIUM PRINTING.

If gelatin be placed in a cold solution of an alkali dichromate, the body swells, behaving in the same manner as when immersed in water. If the swollen mass be dried and kept in the dark without special precaution, no alteration takes place which materially affects the properties of the gelatin except after some hours. The period of immunity from change largely depends upon the temperature and the amount of moisture present in the mass. In warm and especially during damp weather, a material change may take place in 12 hours, and the result of that change is that the gelatin has reduced some of the chromium salt, the mass has lost its yellow colour becoming dull orange, its absorption capacity for water, and the increase in volume consequent, is lowered, and the temperature at which the body when swollen in water passes from the 'gel' to the liquid state is raised. As time goes on, the changes in the normally dry chromated mass increases, with the result that the gelatin almost wholly refuses to absorb water, and it will not dissolve at increased temperature—the gelatin has become insoluble.

If the dichromated gelatin be kept in a cool and dry atmosphere it will remain practically in its original state for several days; and with complete desiccation, no change of moment can be observed after many weeks' storage.

The change in appearance and behaviour thus indicated proceeds with great rapidity in the presence of light, provided that the dichromated gelatin is ordinarily dry. In the moist state the alteration is extremely slow. Gelatin may therefore be said to form in conjunction with a dichromate a mixture sensitive to light. What is true of gelatin holds good for many other substances: for example, to its parent *collagen* and to its primary degradation product *gelatose*, to albumen, gum arabic, and to starch. All these substances reduce alkali dichromates in the dark, but more rapidly in the presence of light, and yield residues which are insoluble in hot water. Many bodies akin to those instanced—gelatin peptone is important in this respect—reduce dichromates but do not yield insoluble products. The feature which it is important to notice is the change in solubility in water and the properties which accompany this change, for upon these the interest and value to the photographer and to the photo-mechanical worker depend.

This change in solubility finds its most important application in the 'carbon' or 'autotype' process, which is one of the most perfect printing methods employed by the photographer, both on account of the faithful rendering of the gradations in the negative and the variety of effect which may be produced. In order to obtain pictures by this process, a sheet of paper coated with dichromated gelatin containing in suspension a suitable pigment, is exposed under the negative. The gelatin becomes changed according to the degree of exposure to light, which is determined by the opacities of the different parts of the negative, and such changed gelatin is insoluble in water. If after exposure the sheet be treated with hot water, the unchanged gelatin is removed and the insoluble portions remain. Inasmuch as the insoluble gelatin remaining upon the paper contains uniformly suspended pigment, it follows that the picture tones will be formed by varying amounts of such pigment, the gelatin acting now as the vehicle. The term 'carbon printing' had its origin in the fact that lampblack was used as the pigment, and this body is still employed in many forms of the sensitive paper or 'tissue.'

The sensitive tissue prepared for the process, is made by coating the surface of suitable paper with a mixture of gelatin, sugar, and colouring matter in water to which an alkali dichromate is added. The machinery employed for the purpose is simple in character, the paper being merely drawn across the surface of the mixture, which is kept liquid by heat, the speed of travel with any preparation determining the thickness of coating. The paper is afterwards suspended in a room through which a current of air is passing. After drying, the tissue is sensitive to light. If the dichromate be omitted, insensitive tissue results. Both forms are manufactured in large quantities. Tissue is produced in a large variety of colours, and care is taken by the makers to use only pigments or mixtures of pigments which are permanent in light. When such rule is followed, carbon prints are perfectly permanent. The insensitive tissue may be sensitised by immersion in an aqueous solution of potassium dichromate after which operation it is dried. The concentration of such solution, which varies between 1 and 5 p.c., exercises a marked influence on the character of the print, the contrast decreasing as the amount of dichromate is increased.

When the sheet of sensitive tissue is exposed under a negative, all portions of the surface of the tissue, except those under absolutely opaque parts of the negative, are changed, and there is formed therefore a skin which is insoluble in water. Such skin acts as a protective coating against the action of the warm water used in removing the soluble portions in development. If such an exposed print be placed in warm water the soluble layer remaining under the exposed portions, viz. that in contact with the paper, dissolves, and there is then nothing to hold the insoluble parts, which therefore leave the paper and no picture is produced. How to meet this difficulty was one of the problems in the early stages of the development of the process. Such difficulty is now avoided in a simple manner. If the exposed sheet be placed in cold water together with a sheet of glass and the gelatin surface (which was in contact with the negative) is fixed upon the glass and the two are afterwards pressed together by means of a squeegee so as to exclude all air, the gelatin paper will, after standing, adhere tenaciously. If the tissue so mounted be now placed in hot water, the paper can be stripped away and will leave the gelatin mass adhering. By gently laving the soluble gelatin washes away, leaving the insoluble gelatin behind. This picture forms a transparency, and such are of considerable value for the various purposes for which positive pictures upon a transparent base are required. If instead of using plain clean glass a sheet which has been polished with a cloth moistened with a turpentine solution of resin and beeswax is employed, the dried picture may afterwards be transferred to paper by the simple expedient of pressing into contact a sheet of paper which has been coated with gelatin, the picture surface and the gelatin being moist at the time. On drying afterwards, the paper readily peels away leaving the picture in perfect contact. The first method, when the surface upon which the picture was developed forms the final resting place for the image, is termed 'single transfer;' and the second, when such support (termed 'temporary support') is only an intermediary, the image being transferred to another medium, is called 'double transfer.' It will be seen that in the first case, the image is laterally inverted and if such inversion be objectionable a reversed negative must be used. But in many cases—as for example, in studio portraiture—it is not convenient to make reversed negatives, and so the double transfer process must be used.

In order to secure adhesion of the exposed tissue to the support it is necessary that its outer margin be tacky. The gelatin must, therefore, be unacted upon. This is secured by rendering the margin of the negative opaque either by means of black varnish or by opaque paper applied to the *glass* side. This is termed the 'safe edge.'

When the exposed and moistened tissue is 'squeegeed' down upon glass all air between the surfaces is excluded and they adhere by atmospheric pressure. Any smooth impermeable medium may therefore act as a temporary support. Finely ground opal glass is the most generally used, the white surface being an advantage because it enables the printer to judge when development is complete. The opal receives a preliminary film of wax and resin and upon this surface the carbon tissue is developed. If, however, the film is to remain on the opal this treatment is omitted.

The final support for the image in the double transfer process is generally paper, which is prepared by coating the surface with gelatin containing a small quantity of chrome alum. The carbon image is moistened together with this paper and the two are brought into intimate contact by the squeegee. The two surfaces adhere so tenaciously on drying that when the paper is pulled away from the support the image is found to be firmly attached. Instead of opal glass a temporary support of paper may be used (Sawyer's temporary flexible support), prepared by coating strong paper with a solution of gelatin containing chrome alum, and, after drying, with an aqueous alkaline solution of lac. The paper is afterwards rendered smooth by calendering. Such support is very convenient, and must be used when it is desired to transfer the image to a *rigid* final support. When a reversed negative can be employed, the image may be developed directly upon the paper which forms the final support. Such paper is first rendered impermeable to air by coating with gelatin solution containing chrome alum, and such coating, when dry, is insoluble in the hottest water ever required for development of the tissue.

As carbon tissue shows no visible change on exposure, the time is determined by trial, an actinometer being used, the indications of which serve for subsequent prints, when the correct exposure has once been found. The precise procedure for the production of a carbon print by the simplest process, that of 'single transfer,' is as follows: the negative first receives a safe edge and a tissue is exposed for the correct period. A sheet of transfer paper previously well soaked in cold water is placed in a tank of water at ordinary temperature and the exposed tissue is introduced and this, when moist, is brought exposed side down upon the transfer paper, the two are withdrawn and placed upon a flat surface and squeegeed together, after which they are allowed to stand under slight pressure for 10 minutes. The mounted tissue is afterwards put into water at 35°. When the soluble gelatin oozes from the edges of the tissue, the backing paper is gently pulled away and water is carefully laved over the surface, until the image is fully developed. The print is then rinsed in cold water. It is now placed in a $2\frac{1}{2}$ p.c. aqueous solution of alum for a few minutes, after which it is washed again in cold water and then dried. The dried picture is ready for mounting or may be kept unmounted. The procedure is identical for double transfer pictures developed upon a temporary support. To transfer to the final support the picture is, after drying, soaked in cold water for 5 minutes. The final support, which has been soaked in cold water until quite soft, is placed together with the print in water at 25°, where they remain for a brief period, The final support is adjusted over the image, the two are removed in contact, 'squeegeed,' and allowed to dry, when the transfer paper can be pulled away and will carry the image with it.

Indirect processes for carbon printing. A process termed 'ozotype,' introduced by Manly, enabled carbon prints to be produced without the direct exposure of the tissue to light. A sheet of sized paper is coated with potassium dichromate and a manganese salt and dried. It is exposed under the negative and from the appearance of the visible image the duration of exposure required is judged. The printed sheet is washed in water and dried. A piece of carbon tissue or, as it is termed by Manly, 'pigment plaster,' is soaked in an acid solution of a reducing agent, and this is squeegeed into contact with the print. The combination is allowed to stand, after which the 'pigment plaster' is developed in the same way as an ordinary carbon print. The reducing solution used is composed of copper sulphate, quinol, acetic acid, and glycerol, in water.

Another method due to Manly and largely used is 'ozobrome.' A print from the negative is first made upon silver bromide or upon so-called gas-light paper (*see* page 229) which is thoroughly washed after fixation, hardened in formalin solution, again washed and dried. A sheet of pigment plaster is soaked in a solution of potassium dichromate, ferricyanide, and bromide, and is brought into contact with the face of the bromide print which has previously been soaked in water. The two are squeegeed together and allowed to remain for about 10 minutes. The subsequent operations of development may take two forms. The print may be developed *in situ* on the bromide print, or the acted-upon tissue is pulled away and is squeegeed down upon transfer papers. In both cases, development is the same as for carbon printing. If the latter plan is adopted, the bromide print can be utilised again, if it is well washed and subsequently redeveloped. When the carbon print is developed directly upon the bromide print, the bleached image—which results in the process—is removed by means of a solution of sodium thiosulphate and potassium ferricyanide, followed by washing in water.

Gum dichromate. In this process gum arabic replaces gelatin. The sensitive surface is prepared by coating paper with a solution of gum arabic, potassium dichromate, and pigment. The paper is exposed under a negative and afterwards developed by washing in warm water, the operation of removing the soluble portion being frequently assisted by attrition. In this method, the rendering of gradation is imperfect, but the results in the hands of tasteful and capable workers are frequently very pleasing.

Oil Printing. A sheet of dichromated gelatin-coated paper is exposed under a negative, washed in cold water and dried. It is then soaked in water until the image is in relief, when the print is removed and the superfluous water removed by a clean cloth. If a brush charged with a varnish pigment (lithographic printing ink) be applied to the damp print with a dabbing motion the ink will be taken by the tones of the print in proportion to the degree of insolubility—in proportion to the light action. A slow motion of the brush will deposit ink which may afterwards be partially or entirely removed by a more rapid dabbing action. Inks of different degrees of stiffness are required and much skill is necessary in the inking.

Oil printing is identical in principle with the Collotype process (*see Surface printing processes*).

'Bromoil' is a modification of oil printing due to C. Welborne Piper. A freshly-prepared silver bromide print is treated with a solution which is identical with that used for the ozobrome process (*v. ante*), but containing in addition ordinary alum and citric acid. The print—which is bleached by this solution—is treated with dilute sulphuric acid followed, after washing, with a solution of sodium thiosulphate and is again washed. After removal of the superfluous water, the print is ready for inking (pigmenting) after the manner briefly described under oil printing. A considerable number of modifications of the first (bleaching) solution have been proposed and used.

Bitumen. The changes which are produced in dichromated proteids and carbohydrates are not only utilised in pure photography, but have very important application in photo-mechanical printing surfaces which are described below. Prior to their use for the purposes detailed, bitumen was employed, which did not, however, offer the same opportunities.

Bitumen of Judæa (*see* vol. i. p. 314), if exposed in thin films to light, becomes so changed that it no longer dissolves in turpentine, and this enables it to be used in the making of line and half-tone relief blocks and in photo-lithography. A solution of bitumen in benzene is applied to the surface of a polished zinc plate, and after exposure under a suitable negative is treated with turpentine. The unexposed parts dissolve away, leaving an image in insoluble bitumen, which is capable of protecting the metal from the action of the mordant and furnishes therefore the means for etching into relief as described under the heading of *Line etching*.

If the bitumen, as it occurs, be powdered and digested with ether, a portion of the mass is dissolved leaving an insoluble residue which is soluble in turpentine. A solution made from bitumen so prepared yields films of a much higher degree of sensitiveness than ordinary bitumen. In spite of this and of other methods (combination with sulphur) for enhancing the sensitiveness, the body is relatively insensitive as compared with dichromated mixtures and is now practically out of use except for certain photolithographic processes.

SURFACE PROCESSES.

Photo lithography. A lithographic print is a picture in varnish-ink produced from the surface of a calcareous stone. Ordinarily, the design upon the stone which produces its selective attraction for the ink upon the inking roller is produced by drawing upon the surface with a fatty medium, but the original design may be copied by photography and transferred to the stone from which prints may afterwards be produced. Such copies are photo lithographs. Any drawing in pure line or in continuous tone may be reproduced in this way. Two methods are adopted—direct and transfer. The negatives most suitable for the production of prints in line are made by the collodion process. The negatives must be reversed. For the 'direct' process the surface of a well-polished lithographic stone is warmed and is then coated evenly with a solution of fish glue (or albumen) and ammonium dichromate in water. The film should be thin. After drying the stone is ready for exposure. For *small* subjects an ordinary glass negative may be used, which is pressed into contact in a specially constructed frame with plate glass front. It is more satisfactory, and is indeed necessary with large sizes, to use thin film negatives, which may be arranged on the plate-glass bed of the frame over which the stone is then placed. To avoid the cost and inconvenience of larger frames, the film negatives may be gently 'squeegeed' into contact with the sensitive surface, using as a cementing medium a solution of mineral oil in naphtha, all traces of which may afterwards be removed by treatment of the surface by naphtha, followed by benzene, without damage to the exposed sensitive coating. The film negatives which should be *collodion* films, strengthened before removal from the glass plate by coating with a solution of rubber in benzene have no 'spring' and adhere easily.

After suitable exposure the surface of the stone is coated by means of a composition roller with a thin film of lithographic *transfer* ink thinned with turpentine or naphtha. After evaporation of the solvent the surface of the stone is flooded with water. On gently rubbing with a tuft of cotton wool the unaffected portions of the coating wash away carrying their covering of ink, and there remains an image of the insoluble fish glue bearing upon its surface the coating of the fatty transfer ink. The stone is then covered with a solution of gum arabic in water which is allowed to dry, after which it is *preferably* allowed to stand for a few hours, when it is ready for the lithographic printer, to be 'rolled up' with lithographic printing ink, dusted with resin which adheres to the ink image, etched with very dilute nitric acid, 'washed out' with turpentine and again rolled up with ink, when an impression may be taken in the lithographic press. Corrections and additional matter may easily be put upon the stone. The effect of the treatment to which the stone has been subjected has been to form upon its surface an image in fatty salts of calcium. This image rejects water whilst the unaffected portions of the stone hold water. If while the surface is in a damp condition, varnish ink (pigment and linseed varnish) be applied, such ink will be deposited upon the image but not upon the damp portions of the stone where no fatty salt has been formed. This, in brief, is the leading principle in the production of an image by lithography. If paper be laid down upon the inked surface and pressure be applied, the ink is transferred to the paper, and the cycle of operations—damping, rolling, and printing—is repeated for subsequent copies.

If the original picture to be copied be in continuous tone, a ruled screen negative (*see Half-tone screen process*) of a particular type is made, which is used for printing upon the coated stone as described. Such process requires considerable attention to details, especially in the selection of the stone and preparation of the negative, and finds its most useful application, not for monochrome, where the copies tend to show a flat scale of gradation, but for photo-chromo lithography, in which a number of separate impressions in different coloured inks from different stones are superimposed, after the manner of the chromo-lithographer for the production of pictures in colour from an original in colour.

In the transfer process a sheet of paper surface coated with gelatin (photolitho paper) is immersed for a few minutes in a 5 p.c. solution of potassium dichromate and afterwards dried in the dark, preferably in a freely moving current of air, in order to ensure rapid drying. It is then printed under a negative (unreversed) of the subject in line to be copied, care being taken to ensure perfect contact of paper and negative, and to avoid undue exposure to light, which causes increase in the thickness of the lines forming the image. After exposure, the sheet is placed on a flat surface and coated with 'transfer' ink by means of a roller, avoiding excess. After evaporation of the solvent, the inked sheet is placed in water at 16° (approx.), where it is allowed to remain for a few minutes, when it is removed and placed face upwards upon a sheet of glass. The unexposed portions of the gelatin absorb water and swell; such action does not take place in the exposed parts to more than an appreciable extent. Upon gently rubbing with a tuft of moist cotton wool, the ink will leave the swollen parts but adhere to the exposed portions. When this process of development is complete there will remain an image of insolubilised gelatin bearing a coating of ink, upon a ground of clean gelatin. This picture—the transfer—is then allowed to dry. It is afterwards damped, when the ink image may be transferred to stone by the usual procedure.

Transfers produced from screen negatives for the production of subjects in continuous tone are only satisfactory when the negatives are made with coarse screen, owing to the tendency of the dots to spread, first in the exposure, afterwards in the inking, and finally in the transfer process.

The advantage of the direct over the transfer process lies in the avoidance of stretch, a necessary consequence with paper, but in ordinary routine work the transfer process is the method most generally used.

Photo lithography in tone. A process for the production of continuous tone subjects—nature negatives and copies of drawings—depends upon the fact that if the thickness of the gelatin coating upon a gelatin 'transfer' paper be increased and contain in addition to the dichromate other substances as, for example, sodium chloride and potassium ferricyanide, the film, after exposure under an ordinary negative and soaking in water, will swell and reticulate in varying degree according to the amount of light action produced under the different portions of the negative. This reticulation of the surface of the transfer means that the film will no longer be continuous in one plane but broken up into 'grain,' and if ink, transfer ink for example, be applied, it will adhere to the image in isolated masses of varying size, which are capable of producing the illusion of shading. The 'grain' can be varied to suit the subject; and the finer the detail to be rendered, the finer the 'grain' should be. The ink image is eventually transferred to stone (*v.* also *Collotype*). From the finished stone, transfers can be taken which can be utilised in the production of a series of new stones, which after careful modification by hand can be employed in the production of pictures in colours by chromo lithography.

Photozincography and photoalagraphy are processes in which zinc and aluminium are used in place of the lithographic stone as the printing surface, and the methods employed are similar to those described.

Collotype. A collotype print is a picture in varnish ink obtained from the surface of chromated gelatin which is supported upon a rigid body, generally glass. Such a surface is produced by exposing the dichromated gelatin-coated glass under a negative and afterwards removing the unaltered chromium salt by washing in cold water, when the film is dried spontaneously. If the film be afterwards moistened with an aqueous solution of glycerol and ammonia, such solution will be absorbed, and the gelatin will swell slightly. If the excess of such 'damping' solution be removed and a charged roller be passed over the surface, the ink from the roller will be taken by the different parts of the film proportionally to the amount of light action which has taken place during the exposure under the negative, and this ink may be readily transferred to paper by simple pressure. By this process it is therefore possible to render automatically by purely chemico-physical means the gradations of light and shade in the negative in such a form as to be utilisable in the printing press. It is interesting to compare this process with Woodburytype, where the translation is mechanical, and with the half-tone block process, where it is produced by optical means.

Provided that a suitable negative be made, any subject can be rendered in collotype. The plates may be printed in the press, where the manipulations are wholly by hand, or in the machine, where the damping, inking, and printing are mechanical. The rate of printing of the best class of collotype is slow. The process is valuable for the reason that it is capable of yielding pictures the gradations of which are faithful to the negative and, as compared with the half-tone block process, without the disturbing effect of the regular dot formation. The variety of printing paper that can be used is considerable, and because of this fact the process has additional value.

For the preparation of the printing surface a sheet of plate glass, $\frac{3}{8}$ to $\frac{5}{8}$ inch in thickness is finely ground upon its surface and is then flowed over with a solution of an alkaline silicate and white of egg. After evaporation of the water, the plate is heated to about 60°. It is then cooled and washed in cold water and afterwards allowed to dry. This process is termed 'substratuming,' and its purpose is to cause a deposit of silica upon the glass. This deposit, in addition to the roughness of the glass, causes the subsequent film of gelatin to adhere strongly. This device is necessary owing to the mechanical strain upon the film caused by the operations of rolling and printing.

The sensitive film is produced by coating the plate with a solution of gelatin and alkali dichromate in water. The gelatin used must be of high grade and of medium 'hardness' and free from fatty matter. The prepared glass is warmed and levelled, and the requisite quantity of the solution is poured upon the surface and spread, preferably by the clean finger. Drying must take place by evaporation at an elevated temperature—there is no intermediate setting to form a 'gel.' Upon correct conduct of this drying the success of the plate maker largely depends. To this end, the plate rests upon levelling screws in a drying oven, which is a box—generally constructed of wood—large in volume, and kept at the suitable temperature by means of a steam or hot-water radiator. Gas or oil heating may be used, provided that care is taken to prevent the products of combustion entering the chamber containing the plates. The construction of the oven must be such that there is no internal vibration and that there are no 'draughts.' Failing these conditions the film will dry with an uneven surface—a fatal defect. The top of the box must be covered with a fabric which will permit the passage of the water vapour from the plates out of the oven.

The oven temperature, varied between 40°–60°, influences the character of the film. When the film of gelatin is dry the oven is allowed to cool, and afterwards the plates are removed and are kept in the dark. The films will remain in good condition for 1–2 days, depending upon the atmospheric surroundings. If, however, storage takes place in an artificially dried atmosphere, as in a storage box containing a tray full of calcium chloride, the plates may be kept 5–6 days. Deterioration is due to spontaneous insolubilisation of the film. For collotypes, laterally inverted negatives are required. In practice, the plates are printed (exposed), in the case of small pictures, from glass-plate negatives. More perfect contact between the surfaces is obtained by printing from flexible film negatives prepared for the purpose, which are laid upon the plate glass bed of the printing frame. By means of thin tin foil such negatives are masked at the margins to show only the amount of subject required. Exposure takes place in the ordinary way, but the frames have usually no backs, so that the under side of the film may be examined in order to observe the progress of printing. The film darkens in proportion to the duration of exposure. Usually, the printer determines the correct amount required by judgment. When the plate has been exposed sufficiently, it is removed, and is then quickly and evenly immersed in water or it may be flooded. Washing continues until the free dichromate is removed, when the film will be practically without colour. It is then dried. Examination of the plate before drying, at this stage, shows that the image is in slight relief and that it is reticulated. A certain amount of 'grain' is required to ensure successful printing at the press, but such 'grain' should not be obvious to the unaided eye. The following conditions influence the character of the 'grain':

kind of gelatin; thickness of film; proportion of dichromate present; the particular alkaline dichromate used; drying temperature; length of time the plates have been kept previous to exposing under the negative; the after treatment of the exposed and washed-out plates and the addition of special salts, as, for example, calcium chloride and potassium ferricyanide (*v.* also *Photo lithography in half-tone*). For special purposes—for example, amongst others, the means of making transfers for halftone lithography—plates are sometimes prepared to give a coarse 'grain' by the addition of the last two named substances, although this is not the only method, nor are they when used the sole determinants.

Printing. The plate during printing must be in a damp condition. This may be secured by simple water damping, but when water alone is used, frequent application is necessary, which makes print making a slow process, and moreover is useable only for hand-press print. Generally water containing a hygroscopic substance as, for instance, glycerol or calcium chloride, is used with addition of ammonia which softens the film. When the film is in a sufficiently moist condition, the superfluous solution is removed, the plate is ready for the press or machine. During printing, the damping solution is reapplied to the ink-free film as required from time to time.

The printing inks used must be specially prepared from *finely ground* lakes and other suitable pigments. No body of a gritty character should be used. The medium should be linseed varnish of high quality: non-drying oils and fatty matter must be avoided. As the film of ink allowable upon the image is very thin, the medium should be 'loaded' with pigment and in consequence collotype inks of high grade are very stiff. For use, the printer employs as reducing agent when required 'middle' and 'thin' linseed varnish.

The rollers used are leather, 'nap' and smooth, and also gelatin composition. A nap roller, charged with stiff ink, is applied to the plate and with frequent rolling the dark and middle tones are produced, after which the smooth leather or composition roller, covered with thinner ink, is used for the more delicate gradations. After inking, the ink from the plate is transferred to the paper (or sometimes a fabric) by pressure. The paper used must be of absorbent nature and of medium hardness. Given these conditions, considerable variety is possible.

Collotype in colour. If the grain of a collotype plate is fairly pronounced, it is possible to transfer a printed image to a lithographic stone, and by such means beautiful colour work has been done. For such productions, plates are specially prepared from negatives which have received considerable modification (by retouching and masking), so that the gradations are made to coincide as far as possible with the amount of particular printing colours required for any region, when superimposition of the different printings will yield the hue required. The stones forming the series for any picture require considerable correction at the hands of a competent lithographic draughtsman, and it is largely owing to his skill that good results are due; hence the process, although interesting, is little used.

Another method is to print from several plates in separate colours from different negatives which have been modified by hand work, superimposing the coloured impressions. The most perfect method where collotype is used is to produce one or two of the necessary printings from collotype plates, generally in neutral tints, and to complete the picture by hand-drawn lithographic stones. This process yields in skilful hands beautiful results. Collotype has been employed also in the three-colour process—for which it is, *ab initio*, unsuitable.

Collotype pure and simple, by reason of the fact that a printing surface of damp gelatin is used—which is liable to be affected by changes in the hygrometric condition of the atmosphere—is a process difficult to work so as to produce very uniform results. Whilst slight variations are not serious in monochrome printing they become so when colour work is attempted. For this reason, mainly, collotype in colours is difficult and in consequence the products are relatively costly.

RELIEF PROCESS.

In the pictorial representation of any object the form is rendered either by pure line, as in simple pen and ink drawing where the lines may be assumed, for simplicity's sake, to be all of uniform depth of colour, or by patches of pigment of varying intensity, either in monochrome or colours, as in a wash drawing or in an oil painting. The former may be termed 'broken' tone and the latter, 'closed' or 'continuous' tone. A third division is formed by a combination of both these methods—a picture may be formed of washes of pigment in conjunction with pure line. An impression in printer's ink from a forme of type matter (the page of this book for instance) is an example of broken tones: the transition from ink to paper is abrupt. A photographic portrait is in continuous tone, there is no discontinuity in the shading by which the form of the person and surroundings is represented.

Pen drawings, the copying of which forms a very important part of the work of the photo engraver, are not always strictly 'broken tone.' In certain cases they are so, as for example, in the so-called mechanical drawing, where the lines are of uniform intensity, and also in many other expressions of the pen of a formal character. Of these it is possible to produce facsimiles, but in work of a more æsthetic character, the definition given does not apply, for the reason that there is shading even in the lines themselves and much of the beauty of the drawings depends upon such variation. The ordinary process of line engraving renders drawings of this character imperfectly, for in the rendering, the forms of the lines only are given, and not the variation in their tone. All the lines in the drawing are reproduced in the printing block, correct in form, in relief and in the same plane. When the printing roller passes over the surface all the lines receive ink to the same amount for equal area, and this ink is eventually delivered to paper. The consequence is that lines of different intensity in the original are represented as the same intensity in the copy, with falseness of effect as a result. It is possible by modifying the lines in the etched relief plate by means of the graver to vary the area of metal and thus to vary the amount of ink delivered to the paper, and in this way to alter the intensity of the printed line. For example, a line which prints too dark may be reduced in width, may be split or cut up into dots. In any of these alternatives the effect will be to show a lighter tone in the print. By such means a facsimile of the *effect* of the drawing is possible, so that to the eye the copy *appears* as the original drawing. In order to produce a rendering of the continuous tones or shading of a wash drawing or a nature photograph by means of a type-high printing block, it is necessary to have recourse to a device. This device depends upon the fact that if there be placed upon white paper a regularly disposed series of black dots, the assemblage when examined at such a distance that the angle subtended by the major diameter of the individual dot is exceedingly small, the eye is unable to distinguish between dot and interspaces and, as a consequence, the illusion of a shade of grey will be produced, the depth of the tone depending upon the proportion borne by the area of the black to the area of the white. If the dots are disposed with perfect regularity and are uniform in size, then the tone produced will be uniform over the area, but any variation either in disposition, size, or intensity of the black dots, will result in tone difference. Assume, for the moment, that blackness and disposition are uniform, then variation in size will admit of there being produced a variation in the shading. If a series of tones, say a simply gradated patch of black to white, produced by washing lamp black upon white paper, be imitated in effect to the eye, by applying the foregoing principle, the ‘ continuous ’ tones of the patch are said to have been translated into ‘ broken ’ tone. The effect in the case of the lamp black wash is due to varying absorptions of the incident light by the varying amounts of the pigment; but in the other instance, the effect is produced by an illusion—by the optical dilution of white with black to produce different shades of grey. The use of this principle is common in graphic representation. It is used by the pen draughtsman; its effect is seen in steel engravings, in the stipple work of the lithographer and in the shading produced by the juxtaposition of mechanically engraved lines of uniform or varying width and distance apart, which the wood engraver employs, for example, in the pictorial representation of machinery.

Given the dot translation of the graded black and white patch, it may be photographed in the same manner as a line drawing and a type-high block produced in similar fashion.

Prior to the period when the modern method for the rendering of gradation was introduced, broken tone pictures were prepared to give a semblance of shading by a method of drawing upon paper having a paste coating which had been impressed with a grain, regular or irregular, while the surface was in a plastic condition. The draughtsman drew upon this surface with a lithographic crayon, simulating the shading of the original drawing, which was possible by varying the pressure upon his crayon. The absence of planarity in the surface gave isolated patches (irregular dots), instead of smooth tones, which would have been produced had the surface been flat. The finished drawing could now be photographed, transferred to metal by printing by the dichromated albumen process, and afterwards etched type high, or the drawing so made could be treated as a lithographic transfer—the image could be transferred to stone and printed lithographically or to zinc and printed in the same way. Again, if it was transferred to zinc of suitable thickness, it could be etched into relief and printed by letterpress.

Another phase of the same plan consisted in employing chalk-coated paper upon the surface of which was printed a series of fine lines close together, or a fine, regular, or irregular stipple in black in addition to the impressed grain. These were known as ‘ scraper boards.’ The surface of the sheet presented, when examined at the normal distance of vision, a uniform light grey tone. Drawing was effected in the way described, and the coating could be scraped away, so lightening any part. The printed tint saved work in drawing. All parts of the board not touched by the draughtsman remained in semi-tone and this, when contrasted with the high light and shadow, gave the opportunity of suggesting the presence of middle tones by the expenditure of less labour in drawing than would have been necessary had the tint been absent. Scraper board was, at one time, employed for the majority of fashion plates and other drawings for commercial purposes. The illustrations, Figs. *a*, *b*, *c* (Fig. 9), are slightly enlarged representations of portions of drawings produced by this method.

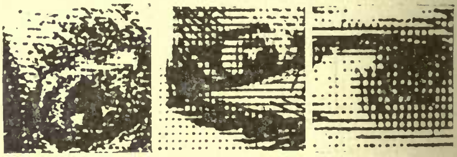


Fig. 9.

Modern photo engraving, however, dates from the introduction of a more facile method of translation, which is the optical method of Ives. Such translation is effected in the negative in the manner to be described.

Processes.

Line. The initial stages in the production of a relief block of a line or other ‘ broken ’ tone drawing are identical with those for the making of a direct photo zincograph (*v. ante*, *Photolithography*) and are directed to the making of a fatty ink image upon the surface of a sheet of zinc. Provided that the metal be sufficiently thick, the image produced for lithography (actually *zinco*graphy) may be etched into relief, or the image produced for relief will serve equally well as the starting-point for lithographic printing.

The processes of line etching now in general use are known by the names of the ‘ roller ’ process and the ‘ dragon’s blood ’ process. Both of these require a print upon the surface of zinc which is prepared by exposing the metal, coated with a very thin film of albumen (or fish glue) and an alkali dichromate, under the negative of the drawing. The exposed print is covered with a thin film of greasy ink, the plate developed in water, and when dry the image is dusted over with finely divided bitumen, which adheres to the ink lines. The excess of the powder is then removed, leaving the metal clean. The plate is now warmed, when the bitumen melts and incorporates thoroughly with the ink. The resist which results is satisfactory for the roller method, but for the 'dragon's blood' process the 'transfer' ink used for coating the exposed albumen plates is replaced by a harder and more wax-like ink, and the resist produced is capable of standing a more prolonged etching, which is an advantage in that more relief is produced with which to commence the characteristic operation of the process. The enameline process (see *Tone process*) is also used for the making of the resist for dragon's blood etching. In the roller method, the procedure, after the resist is made, is as follows: The plate is placed for a minute or so in a 1 p.c. solution of nitric acid for the purpose of removing any traces of dirt from the bare parts of the metal, after which it is washed and then wiped over with a sponge charged with a solution of gum arabic. The plate is now rolled up in the lithographic manner with a roller charged with the so-called 'starting' ink which is usually composed of letterpress ink, beeswax, and lithographic varnish. When the image is strengthened by this 'rolling up,' the plate is dried and is then dusted with resin—usually dragon's blood is used—after which the plate is again placed in dilute nitric acid, where it remains until a slight relief is obtained for the covered parts of the metal. The plate is washed, dried, and heated slightly, the effect of which is to cause the wax in the ink to run over the exposed edges of the lines—an operation requiring skill and experience—and the plate is then cooled.

This cycle of operations is repeated usually four times, increasing at each repetition the concentration of the acid, the amount of ink, and the degree of heating of the plate. After the operations described are completed the plate is cleansed. Examination will show that the lines in relief have sloping sides with a step-like formation as shown in Fig. 10. The 'steps' are due to the successive meltings of the ink and subsequent etchings, and are only slightly evident if care and skill are employed by the etcher. These steps are to be removed so that the lines may have smooth sloping sides. If the running of the ink has not been properly performed so that the sides are unprotected, they will be eroded or undercut, and as a result the lines will break away in the etching bath or at the least be defective and an imperfect rendering of the drawing will be given. The steps or 'shoulders' to the lines are removed by the operation of 'finishing.' A hard, glazed leather roller is charged with a strongly resisting ink (composed of good lithographic printing ink, beeswax, and bitumen) and with this a thin film is applied to the surface of the lines of the previously cleaned plate, after which the plate is placed in dilute nitric acid. This removes the 'step' near the surface of the line. The plate is washed and dried and again rolled up, but this time the roller is pressed down during rolling so as to coat the straight edge of the side of the line left by the first finishing bath and the plate is again etched until the remaining 'shoulder' is removed.

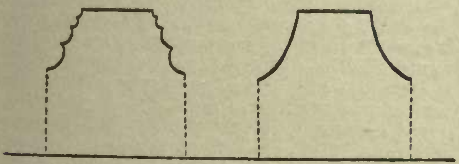


FIG. 10.

In the dragon's blood process, the plate is given a first etch for a longer period than in the roller method. The subsequent protection of the sides of the lines is effected by what is called a 'banking' of the resin. This banking is made by brushing across the plate, by means of a large flat brush, finely powdered dragon's blood which is, by reason of this operation, mechanically held against that side of the line which faces in the opposite direction to that in which the brush is travelling. The amount of banking is varied by the angle at which the brush is held. When the excess of resin is removed the plate is *gently* heated, when the resin melts sufficiently to stick to the metal, after which it is cooled. The 'banking' is repeated from the remaining three sides of the plate, so that every line, in no matter what direction it may be, receives protection. In some cases, extra 'bankings' may be wanted. The plate must not be heated sufficiently to cause the resin actually to flow. After the sides of the lines are protected, the plate is etched, when the banks of resin gradually break away and the edges of the lines begin to be exposed. The plate is washed, dried, and the protection of the sides again performed, and the etching repeated. These operations are continued until sufficient relief is obtained. To secure adequate protection for the surface of the lines, the plate is usually rolled up once with a resisting ink, the resin afterwards adhering to this, and when the plate is heated incorporating with it.

After the main etching, the plate is cleaned, and then may require a 'finishing' bath, but the 'finishing' is not required to the same extent as in the plates produced by the roller process.

Etching is generally performed in large earthenware troughs supported upon rockers, by which a see-saw motion is given, but it is becoming now the practice in large establishments to etch by means of etching machines which mechanically deliver a spray or stream of acid against the plate. The etching is more quickly performed, and there are attendant technical advantages. The powdering with dragon's blood may now be done by a special machine.

The advantage of the dragon's blood process lies in its speed and ease, compared with the roller method.

Where there are large areas of bare metal, it is necessary to obtain considerable depth, the actual depth being mainly dependent upon the width apart of any two contiguous ink-bearing portions standing in relief. The removal of the metal by etching is lengthy, and is, moreover, wasteful of nitric acid. In modern practice, it is the custom to avoid, as far as possible, this 'deep' etching by removing the metal in the more open spaces by means of a rapidly rotating cutter in the 'routing' machine.

The etched plate is afterwards trimmed, and is then mounted upon a block of oak or mahogany 'type high,' when it is ready for the printer. The satisfactory mounting of the plates is one of the most serious problems of the block maker, there being at present no entirely good method.

Tone processes ('half-tone' or 'process' blocks). In these processes we use the principle of translation of continuous tone into broken tone described. Any picture, whether drawing or photograph, may be represented by the half-tone process, which is the most common of modern illustration methods. Given a picture, such constitutes the starting-point, but if an object in relief is to be portrayed, an ordinary photograph must first be made. Except in certain cases—where the range of contrast in the subject is slight—this is the rule. Such photograph is the original. A secondary negative is now made—the original is again photographed—and it is in this second photograph that the translation of tone is made into dot and from this negative the metal printing-surface is produced.

To produce the half-tone negative there is placed, some little distance in front of the sensitive plate, during the exposure in the camera, a sheet of glass having a large number of small apertures, the effect of which is to translate or break up the shading of the ordinary photograph or drawing into dots of various sizes in proportion to the brightnesses of the tones. This glass plate is termed the 'ruled screen.' It is formed of two plates of flat transparent highly polished glass which are cemented into optical contact. These have, upon their inner surfaces, a series of alternate opaque and clear lines which are usually of equal width, and their direction forms with the sides of each plate an angle of 45°, but from different sides with the two plates. The result is that when the plates are in contact there is produced a series of square transparent openings. The number of lines to the linear inch with different screens varies from 50–250 and as the spaces and lines are equal we have lines equal to $\frac{1}{100}$th to $\frac{1}{300}$th in. The effect produced by the different rulings when the screens are used for negative making is to give a variable number of dots to the superficial inch, each dot corresponding to an opening. The greater the number of dots upon unit area the finer the gradations (detail) in the translation. It may, however, be taken that for few subjects is it necessary to use screens having rulings finer than 175 lines to the inch.

Such screens are made by coating the surface of glass with a resisting medium which is afterwards cut through by means of a diamond point in a special form of ruling machine leaving the glass exposed. Afterwards the plate is subjected to the action of hydrofluoric acid, the resisting medium is cleared away, and the etched lines are then filled in with a black pigment. On completion, there is shown a series of opaque lines upon a transparent ground. Two such plates cemented in contact form the screen, the appearance of which is shown by Fig. 11.

The placing of the screen is not a matter of simplicity, so far as its distance is concerned. It is necessary that the position be chosen after consideration of the camera extension, the lens aperture, the screen ruling, the subject and the negative-making process, which is most usually wet collodion. If the screen be placed in close contact, dots will be produced, but they will be of equal size, and all gradation of tone will be lost. The dots will also be variable in density with this uniform size while they should be variable in size and uniform in density. If the screen be placed too far away the sizes of the dots will not be correct. In the case of too great distance, the effect of the screen for some tones will be lost, the tones will be continuous again and if a further distance than this be taken the effect of the screen will be wholly lost. In such a position the screen acts, to all intents and purposes, as a sheet of neutral-tinted glass. The success of the process in practice depends, after correct distancing of the screen upon exposure (which is made in part with one aperture of small size and in part with one of much larger opening—a plan which is necessary in all cases where there is any considerable range of contrast in the original) and upon the processes of development, reduction or clearing and intensification which follow.

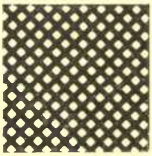


FIG. 11.

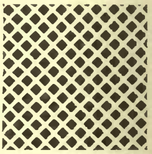


FIG. 12.

From the negative the print upon metal, which is to form the resist to the etching mordant, is prepared. Usually, for the best class of work, half-tone blocks are prepared upon copper, and the process employed is that known as the 'enameline' or 'fish glue' method. A sheet of polished copper is coated with a viscous solution composed of fish glue (gelatose) and an alkali dichromate in water, and the resulting film is dried by gentle heat. The coated plate is exposed under the negative, when the portions exposed to light change and become insoluble in water, whilst those parts under the dots remain unaffected and so retain their solubility. After exposure, the plate is washed in cold water until all the soluble portions are removed when the plate is dried. There is now on the surface of the metal a print, the tones of which are produced by dots of various sizes. The metal is strongly heated, when the print changes in character, becoming hard and enamel-like, in which condition, when cool, it is capable of withstanding the mordant—ferric chloride—which rapidly attacks the uncovered metal. Upon etching the protected parts are left standing in relief, the necessary condition for the printing press. In most cases, the automatic process is assisted by a process of selective or 'fine' etching. If the tones in any part of the plate are not such as will give the desired shades, if for example, the dots are too large, which means too dark a shade in the print, the remaining portions of the etched plate are covered over by a resisting medium applied by means of a brush and the plate is submitted to a further etching. It will be noted that in the description, no mention is made of any protection to the sides of the dots as the etching proceeds, whilst reference to the explanation of the mode of producing line plates will show that elaborate precautions are taken to such end. The actual 'depth' or 'relief' required in a half-tone block is extremely small, for the reason that the ink-bearing elements—the dots—are very close together. But lateral action does take place, with the result that, owing to under-cutting, the size of the dot portion decreases and as a consequence the ink-bearing capacity is lessened and so the dot prints lighter. Allowance is made for this in the negative, so that the printed dots on the metal are larger than are required in the finished plate. Upon this lateral action, modification of tone by 'fine etching' depends, for, if the re-etching for any tone be carried far enough, the tone may be brought to almost any degree of lightness of shade. After completion of the etching, the plate is cleaned and is mounted type high upon wood.

The continuous tones of a picture may be translated into isolated elements of a less regular order than obtains with the use of the ruled screen, by means of a special form known as the 'metzograph.' This is a plate of glass upon the surface of which pyrobetulin has been deposited by sublimation. The coating so produced takes a vermicular form and the surface is afterwards etched with hydrofluoric acid when the glass assumes a similar character, presenting a series of minute cavities, the number per unit area on the 'coarseness' of the screen can be varied. Such a plate appears to the eye faintly translucent. If it be placed in front of the sensitive surface during exposure, the tones are broken up into isolated particles which are distributed with extreme uniformity but without the mechanical regularity of the ruled screen image. The particles vary in size and shape and the absence of the definite and regular dot formation is an advantage in the reproduction of many classes of originals. The negatives are employed in the same way as those made by the ruled screen. The character of the 'texture' produced by the two methods is shown in Fig. 13, *a* and *b*, by which comparison may be made.

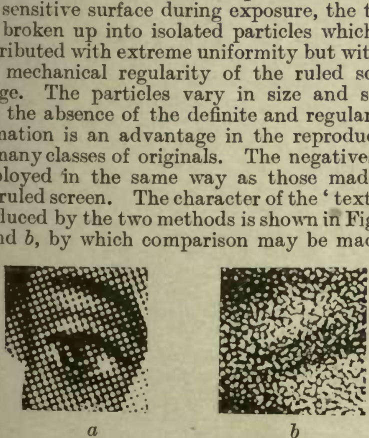

a *b*

Fig. 13.

Three-colour printing by relief blocks. The principles upon which colour is rendered by the so-called 'three-colour' process are given under the heading of colour photography (*v. ante*), and it is only necessary here to show how these principles are utilised in the making of prints by letterpress. Briefly, the method consists in making three negatives through colour screens, one for each of the fundamentals, and from the negatives, blocks are prepared which are printed on the principle of superimposition in inks approximately complementary to the sensation hues.

Two processes are employed, the indirect and the direct. In the former, ordinary continuous tone three-colour negatives are made, and from these transparencies by contact from which the three half-tone dot negatives are produced. Or, in the direct process, the dot negatives are made direct from the object upon special dry plates which are panchromatic (*see Orthochromatic photography*) and also suitable for ruled screen negative making. Frequently such negatives are made upon panchromatic collodion emulsion. There is a slight complication in making the negatives owing to the fact that if there be printed two or more impressions one above the other from half-tone blocks (or indeed from any printing surface where the colour is distributed in the form of elements in perfectly regular order), a pattern is produced—the so-called *moiré* effect—which is very objectionable. This pattern cannot be avoided, but it may be reduced to an almost negligible form if it be arranged that the lines of dots (forming the half-tone picture) in the separate printings cross at a particular angle which is secured by the positions of the ruled screen when the negatives are made. The direct process is only applicable to the photography of flat objects. If the object is in relief the indirect process must be employed. In any case, the negatives forming the set must have images accurately equal in size. Blocks are prepared upon copper by the enamelline process. Successful three-colour work is very largely a matter of skilful fine etching, but the amount required is frequently in excess of that which would be required were more care bestowed upon the making of the negatives. The plates, when finished, are accurately trimmed and mounted, and are afterwards printed in ink of the hues yellow, crimson, and greenish blue. At the present time, the sensitive plates obtainable well fulfil the theoretical requirements, but the same cannot be said of the printing inks.

On the Continent more than in Great Britain and the United States, at the present time, a four-colour process is employed with considerable success. A set of blocks is prepared by the three-colour method and a fourth block is made from the original from a negative made through the ordinary 'yellow' screen, which is employed for the additional printing, the colour being generally a grey of a tone to suit the subject. The extra printing from a block prepared by skilful hands is a valuable aid and serves to soften the crudity of colour which is so frequently a fault in pictures produced by the orthodox three-colour process.

Preparation of drawings and photographs. The translation of any picture by screen methods always leads to a flattening of the contrast. Although 'fine etching' of half-tone plates is to a considerable extent employed to alter the appearance of the pictures as presented by the proofs from the plates—of illustrations, indeed, which are not satisfactory to those who wish to use them even before they are reproduced—the process would, to some extent, be necessary in the case of good originals because of the flattening effect of the screen. When drawings are to be reproduced by these methods and have to be made for the purpose, allowance is generally made for the reduced contrast by forcing the effect in the drawing, hence 'drawings,' for process, which are generally made in monochrome body colour although useful for the purpose intended, are of little value afterwards for obvious æsthetic reasons.

Any drawing in line, even those made without any regard to reproduction processes, where beautiful effect is the only consideration, may be successfully translated, but only by the expenditure of extra time and skill. Disregarding pictorial drawings, much technically unsatisfactory 'copy' is dealt with in the ordinary way. When drawings in line are made, however, with a view to reproduction in the commercial way, they are generally prepared in black line upon white card.

By far the larger amount of half-tone illustrations to catalogues (especially those showing machinery) and publications of a similar commercial character are prepared from photographs which have been 'worked up' by the draughtsman, who changes the appearance of the original by modifying portions, by suppression, or by addition, and this to such an extent that the photograph is completely changed. Such 'working up' is carried out by means of the 'air brush,' a pen-like tool by means of which a fine stream of air can be caused to project a spray of liquid pigment upon a surface, the effect producible being entirely under control, and moreover—which is the important feature—with that smoothness and continuity which is a characteristic of the shading in a photograph, so that the added work is in harmony with the print. It is largely owing to this that the photo-engraver has almost entirely replaced the wood engraver in the preparation of the illustrations for the best classes of catalogue.

C. W. G.

PHOTOLITHOGRAPHY *v.* PHOTOGRAPHY.

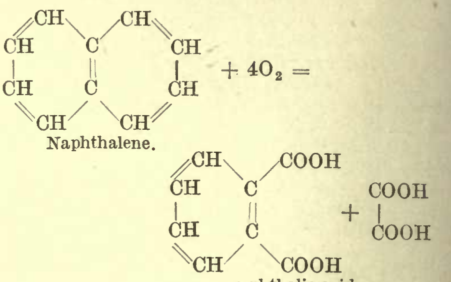
PHOTOPHONE *v.* SELENIUM.

PHOTOSANTONIC ACID *v.* SANTONICA.

PHTHALEÏN DYES *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PHTHALIC ACID. The three dicarboxylic acids of benzene are known as the phthalic acids. Of these the only one of technical importance is *ortho*phthalic acid $C_6H_4\begin{cases}COOH\ (1),\\COOH\ (2)\end{cases}$ and this is the compound which is always understood when the name *phthalic acid* is used without further qualification, the meta-compound being distinguished as *iso**phthalic acid* and the para- as *terephthalic acid.*

*ortho***Phthalic acid** was first obtained by Laurent in 1836 by the oxidation of naphthalene (Annalen, 19, 38), and the same coal-tar product has always served as the chief source of this valuable acid—



Similarly other di-substitution derivatives of benzene containing carbon chains or groups in the ortho- position yield phthalic acid on oxidation, *e.g.* in addition to naphthalene cited above, tetrachlornaphthalene, alizarin, purpurin, *o*-toluic acid, have been employed, along with such oxidising agents as dilute nitric acid, alkaline permanganate, chromic acid, sulphuric acid (Marignac and others, Annalen, 42, 215; 66, 197; 75, 12, 25; 130, 334; 144, 71; 148, 60; Ber. 6, 945; 7, 1057; 12, 579; 18, 1499; Zeitsch. Chem. [ii.], 4, 551,705; Compt. rend. 56, 82; Frdl. 1897-1900, 664).

A variety of other methods are known, *e.g.* the action of potassium ferrocyanide and sulphuric acid on salicylic acid, or of formic and sulphuric acids on salicylic acid; interaction of resorcinol and sodium bicarbonate; by the reaction between benzyl chloride, carbon tetrachloride and nitric acid; or by acting upon benzene or benzoic acid with pyrolusite and concentrated sulphuric acid in the cold.

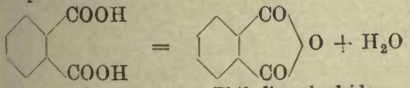
Häussermann (J. 1877, 763, 1158) describes a method suitable for laboratory preparation, from 2 parts of potassium chlorate in 10 parts of commercial hydrochloric acid and 1 part of naphthalene, which mixture is gently heated, chlorination first taking place and then oxidation. The product is washed with water and with light petroleum, and afterwards 10 parts of nitric acid (sp.gr. 1·45) is gradually added and the mixture boiled. When all dissolves, the nitric acid is evaporated and the residue distilled; phthalic anhydride passes over, which may be further purified by sublimation, and reconverted into phthalic acid by boiling with caustic soda and acidifying the cold solution with mineral acid. The precipitated phthalic acid is best purified by recrystallising from boiling water.

Physical properties. It exists in trimetric plates; whole crystals melt at 213°; when powdered, at 203°, passing into the anhydride. Sp.gr. 1·585–1·593; 100 parts of water at 14° dissolve 0·54 parts of acid, and at 99° 18 parts of acid (Graebe, Annalen, 1887, 238, 321). Phthalic acid is readily soluble in alcohol, sparingly so in ether and insoluble in chloroform (hence separation from benzoic acid); it is slightly volatile in steam. The acid shows an absorption band in the spectrum, but the anhydride does not. It is said to form a eutectic mixture with its anhydride (de Stadt, Zeitsch. physikal. Chem. 41, 353). For measurements of conductivities reference should be made to the work of Jones (Amer. Chem. J. 42, 520; 43, 187; 44, 159); Sidgwick (Chem. Soc. Trans. 1910, 97, 1677); Godlewski (Chem. Zentr. 1904, [ii.] 1275).

Chemical properties. Phthalic acid forms a characteristic, sparingly soluble barium salt (Carius, Annalen, 1868, 148, 60; Hermann, Annalen, 1874, 171, 78), and also forms salts with most metallic oxides, including bismuth, yttrium (J. pr. Chem. [ii.] 74, 142; Bull. Soc. Chim. [iii.] 31, 135; J. Russ. Phys. Chem. Soc. 42, 586). Calcium phthalate on heating gives benzophenone, benzene, carbon dioxide, small quantities of other hydrocarbons and anthraquinone. The acid itself, when heated with excess of lime, yields benzene and calcium carbonate, calcium benzoate being formed as an intermediate product. The acid is very stable towards sulphuric acid, merely passing into its internal anhydride with loss of water; more strongly heated it loses a little carbon dioxide and is sulphonated. With sulphuric acid it is also said to form a definite additive compound, $C_8H_6O_4+H_2SO_4$ (Hoogewerf and van Dorp, D. R. P. 21352). Michaelis has prepared a phthalo-arsenic acid $(COOH)_2{\cdot}C_6H_3{\cdot}AsO(OH)_2$ (Annalen, 320, 271).

The *constitution* of the acid has been solved by Nölting (Ber. 1885, 18, 2687) who by oxidising the three xylenes with permanganate obtained excellent yields of the phthalic acids. As meta-xylene forms three isomeric nitro-xylenes, xylidenes and xylenols, ortho- two, and para- only one each of these derivatives, therefore *iso*-phthalic acid has positions 1, 3, ordinary phthalic 1, 2, and terephthalic 1, 4, for the carboxyl groups.

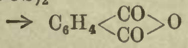
Phthalic anhydride is formed (1) by distillation of the acid, (2) by warming the acid with acetyl chloride (Laurent, Marignac), (3) by interaction of lead nitrate and phthalyl chloride (Lachowicz, Ber. 1884, 17, 1283), (4) by heating phthalonic acid—itself an oxidation product of naphthalene—to 200°, (5) dissolving the acid in phenol, anisole, or veratrole, containing P_2O_5 (Gazz. chim. ital. 30, ii. 361), (6) shaking a solution of sodium phthalate with two molecules of acetic anhydride (Gazz. chim. ital. 26, ii. 482). All these methods are represented ultimately by the equation—



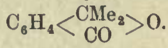
Phthalic anhydride.

o-Phthalic acid is the only one of the three isomerides which gives in this way an *internal* anhydride. A novel method of preparation is given by Denham (Chem. Soc. Trans. 1909, 95, 1235) from the interaction of sulphur monochloride on the sodium salt—

$C_6H_4(COONa)_2 \rightarrow C_6H_4(COOS)_2$


$\rightarrow C_6H_4<{}^{CO}_{CO}>O$

The anhydride exists as long, tough needles, m.p. 128°, b.p. 284°; it is very sparingly soluble in cold, more readily so in hot, water, being gradually reconverted into phthalic acid; in alcohol and ether it is readily soluble, and dissolves in alkalis forming phthalates. With dry ammonia it gives phthalimide (*see* below); with alcoholic ammonia phthalamic acid, $C_6H_4(CONH_2)COOH$, m.p. 149°; and with aqueous ammonia it yields ammonium phthalamate $C_6H_4(CONH_2)COONH_4$, which on heating is transformed into phthalimide (*see* later).

Fusion of phthalic anhydride with lime produces benzene and diphenyl (Annalen, 1879, 196, 48); with zinc dust it gives biphthalyl, $C_{16}H_8O_4$, and with zinc dust and methyl iodide yields dimethyl phthalide  $C_6H_4<{}^{CMe_2}_{CO}>O$. In contact with alkaline hydrogen peroxide it reacts with formation of monoperphthalic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}OH$ and the external anhydride of this. Three molecules of phthalic anhydride combine with 2 molecules of $SbCl_5$ to form a crystalline compound.

The usual method for the detection of small quantities of phthalic anhydride is that of fusion with about twice the weight of resorcinol in presence of a drop of concentrated sulphuric acid. In this way fluorescein is produced (*v. infra*), and the reddish-brown product, when dissolved in dilute caustic soda and poured into a large volume of water, yields a magnificent green fluorescent solution. This reaction is shown by all the ortho-dicarboxylic acids of the benzene series, although with the formation of a variety of coloured solutions, but it is not shown by the meta- or para-dicarboxylic acids. Succinic anhydride shows an analogous reaction.

A method for the quantitative estimation of phthalic anhydride in presence of a number of impurities is described by Boswell (J. Amer. Chem. Soc. 1907, 29, 230). It consists in the careful sublimation of the anhydride and subsequent titration with standardised caustic soda.

TECHNICAL MANUFACTURE.

Owing to the extensive use of phthalic anhydride in the manufacture of synthetic indigo (*q.v.*) and the pyronine and triphenylmethane class of dye-stuffs, a cheap technical process for its preparation in large quantities was essential, and this has been achieved in the various patents of the Badische Anilin u. Soda Fabrik (*cf.* D. R. P. March 31st, 1896, 91202; Eng. Pat. 18221, August 17th, 1896; Frdl. 1894-1897, 164), which are based upon the observation that naphthalene is readily oxidised by concentrated sulphuric acid containing mercuric sulphate, its oxide, or the metal itself, which acts as a catalyst, and that the sulphur dioxide formed by the reduction of the mineral acid is reconverted into sulphuric acid by absorption of oxygen from the air, the whole process being practically continuous.

In the English patent the quantities given are as follows:—

100	kilograms	naphthalene
1500	,,	sulphuric acid (100 p.c. H_2SO_4)
50	,,	mercuric sulphate.

In place of naphthalene, β-naphthol, naphthionic acid, or phenanthrene may be used. The mercury sulphate remains behind as residue in the retort and is used over and over again.

It should be borne in mind that a too vigorous oxidation will destroy the phthalic acid as soon as formed, and therefore the preparation should be conducted within well-defined limits of temperature—about 270°-300°.

A detailed account of the exact conditions employed, with a description of the manufacturing plant, is given below.

In a vertical cylinder fitted with a mechanical stirrer, the following substances are mixed, and agitated for three hours until the naphthalene is completely dissolved :—

3675 kilos. sulphuric acid 66°Bé.
1050 ,, oleum (23 p.c. SO_3 content).
350 ,, naphthalene.

The solution (A) so prepared is stored in a reservoir until required.

The oxidation vessel consists of an iron pan, built round with bricks and carefully heated by means of gas jets. The pan possesses a removable lid, has a flat bottom, a diameter of 6 feet and is 2 feet deep ; a wide tube for leading off the vapours is provided, and through the top passes a shaft connected with a two-arm stirrer, worked mechanically, which just scrapes the bottom of the pan ; also several iron marbles are allowed to rotate on the pan bottom to attract charred matter, and a pressure gauge is inserted on the lid.

The phthalic anhydride sublimes simultaneously with quantities of sulphuric acid which distils over, and these vapours are conducted through a short pipe, 8 inches in diameter, into the condenser, which consists of three concentric lead cylinders fixed one within the other at a distance of about a foot ; two of these communicate with one another through the bottom and open into the third, which is surrounded by an outer condenser, through which water is circulated. The third of these cylinders is again connected with a reservoir into which the condensed sulphuric acid overflows. On the lid of the closed condensers is a vacuum arrangement which conducts off the sulphur dioxide as soon as formed, to an absorption apparatus.

At the beginning of the operation the oxidation pan, containing 120 kilos. of sulphuric acid-monohydrate and 4 kilos. of mercury, is heated for 1½ hours very gently until all the monohydrate distils over, the stirring apparatus being worked during this operation. The prepared solution (A) is now admitted into the pan from a storage reservoir above, in portions of 22 litres, and the gas-heating is so regulated that each 22 litres distils over in about 13–17 minutes. The end of each operation is observed by the increased noise of the rotating marbles on the bottom of the pan, and a further measured lot of 22 litres is then run in.

The process is continued until the pan contains so much charred matter that it is advisable to clean it. The progress of the anhydride formation is controlled by gas analysis, the amount of CO_2 evolved being determined from time to time. When the CO_2 content reaches 0·6–0·8 p.c. the addition of naphthalene solution (A) is discontinued, and in this emergency three times the volume of sulphuric acid of 66°Bé. is admitted and distilled away, after which the vessel is again ready for 2 or 3 days' continuous working. Should the CO_2 gas-content reach 1 p.c., the work is interrupted for a complete cleaning of the vessel ; the pan is heated until perfectly dry, the lid opened, and charred matter chipped from the interor.

To separate the sulphuric acid and phthalic anhydride which together collect in the condenser, the clear sulphuric is first decanted, and then the crude phthalic anhydride is further separated centrifugally and washed free from acid. The product is dried and purified by resublimation in a pan mechanically stirred, and heated over a coke fire. A large cylindrical vessel serves as condenser. The cost of this process, as worked in Germany, is about one mark per kilogramme of phthalic anhydride.

Other less well-known methods which may have some technical value for the preparation of phthalic acid are given below.

O. Imray, of the Basle Chemical Works, took out an English patent, No. 15527, on July 31, 1901, for the heating of naphthols in presence of a very slight excess of alkali, with metallic oxides or peroxides, such as copper and iron oxides or barium, lead, or manganese peroxide, to a temperature of about 240°–260°C. for 8 hours in oxygen gas under pressure. Phthalic and some benzoic acid are formed, together with a few intermediate products (*see* Ber. 1888, 21, 1616). Not only naphthols, but also nitro-naphthalenes, naphthylamines, and naphthalene sulphonic acids may be used (*cf.* D. R. PP. 136410, 138790, 139956, 140999; Frdl. 1902–1904, 112–115).

Many patents have been granted for the use of salts of rare earths as catalysts in the oxidation of naphthalene by means of sulphuric acid. The nitrates, oxalates, carbonates, oxyhydrates, sulphates of cerium, lanthanum, neodymium, praseodymium, ytterbium, have all been used as substitutes for the mercury in the original German patent, No. 91202 (*see* above). A mixture of—

25 grms. naphthalene
375 ,, concentrated sulphuric acid
15 ,, oxide of rare earths

evolves gas gently at 100° and at 200° a vigorous evolution of SO_2 and CO_2 begins and continues briskly until the thermometer registers 270°. Pure white crystals of phthalic anhydride sublime over into the receiver (D. R. PP. 142144, 149677, 152063, 158609). It is claimed that the use of rare earths as a substitute for mercury salts is more economical, as they can always be recovered from the residue in the retort, although the yield is not quite so good as with the use of mercury. A process for the oxidation of naphthalene by electrolysis of a solution of 20 p.c. sulphuric acid and 2 p.c. cerium sulphate is also described (Frdl. 1902–1904, 105–107 ; D. R. P. 152063).

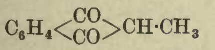
The observation that naphthalene is soluble in boiling water has been utilised by Procházka (Ber. 1897, 30, 3108) for its oxidation to phthalic acid by means of hot permanganate. Almost theoretical results are obtained, phthalonic acid being produced as an intermediate stage. The reduction of permanganate is very rapid, and the best results are obtained when a large excess of naphthalene is employed, the unchanged hydrocarbon being easily recovered ; 100 grms. commercial permanganate yield 17 grms. phthalic acid, the theoretical yield being 19 grms.

The Basler Chem. Fabrik have taken out a patent (D. R. P. 136410 ; Frdl. 1900–1902. 1301) for the manufacture of phthalic acid together with benzoic acid from α-nitro-napthalene and nitrophenols by the action of alkalis under pressure and in a dilution medium such as common salt.

Esters of phthalic acid with most of the known alcohols have been prepared in the usual way. The dimethyl ester distils at 280°/734 mm.; diethyl ester at 295°; diphenyl ester melts at 73°; benzyl acid ester has m.p. 106°–107°, affording a good characterisation of benzyl alcohol; cyclohexanol acid ester, m.p. 99°, neutral ester m.p. 66°. Various esters of phthalic acid are used as solvents for resins, *e.g.* copal resin, which need not be melted to be dissolved (Hesse, D. R. P. 227667).

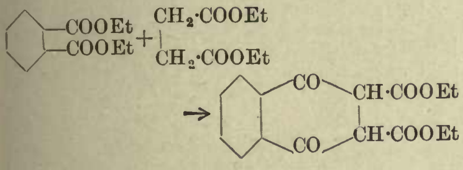
Pickard has accomplished the resolution of various complex alcohols into their optically active components by making the acid-ester by simple fusion with phthalic anhydride and combining this with active bases (Chem. Soc. Trans. 1907, 91, 1974).

Ethyl phthalate reacts with ethyl acetate and sodium to form ethyl diketohydrindene carboxylate; and with ethyl propionate and sodium, yielding methyl diketohydrindene—



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH{\cdot}CH_3$$

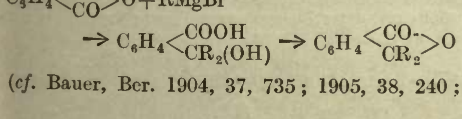
If ethyl succinate be substituted for ethyl propionate, ethyl dihydronaphthraquinone dicarboxylate is formed.



Derivatives and Condensation Products of Phthalic Anhydride.

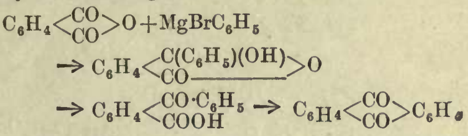
The extraordinary reactivity of the anhydride accounts for the great number of important derivatives which have been prepared. First among these should be mentioned *phthalyl chloride* $C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$, obtained by the action of phosphorus pentachloride. It is a liquid of b.p. 275°/726 mm., solidifying at 0°C. From this, by the action of ethyl alcohol, is obtained the ether, $C_6H_4<\begin{matrix}C(OEt)_2\\CO\text{———}\end{matrix}>O$, while it also condenses with ketones or with ethyl sodioacetate (Fischer and Koch, Ber. 16, 651; Bülow and Koch, Ber. 1904, 37, 577; 1905, 38, 474). Reduction of phthalyl chloride with zinc and hydrochloric acid produces the important derivative *phthalide* $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>O$, m.p. 73° (*v.* LACTONES), and with acetic acid and sodium amalgam the phthalyl alcohol, $C_6H_4<\begin{matrix}CH_2OH\\CH_2OH\end{matrix}$.

Grignard's reagents act on phthalic anhydride, forming the dialkyl and diaryl *phthalides*, of which a large variety have been prepared:—



$$C_3H_4<\begin{matrix}CO\\CO\end{matrix}>O+RMgBr$$
$$\rightarrow C_6H_4<\begin{matrix}COOH\\CR_2(OH)\end{matrix}\rightarrow C_6H_4<\begin{matrix}CO\text{-}\\CR_2\end{matrix}>O$$

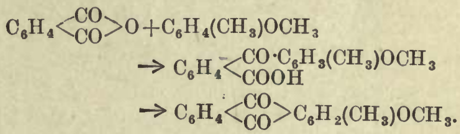
(*cf.* Bauer, Ber. 1904, 37, 735; 1905, 38, 240; Arch. Pharm. 247, 220). Pickles and Weizmann (Chem. Soc. Proc. 1904, 20, 201) have prepared *mono*-aryl hydroxyphthalides by this means, which give by the action of water keto acids; anthraquinone has thus been prepared by the following series of reactions:—



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+MgBrC_6H_5$$
$$\rightarrow C_6H_4<\begin{matrix}C(C_6H_5)(OH)\\CO\text{————}\end{matrix}>O$$
$$\rightarrow C_6H_4<\begin{matrix}CO{\cdot}C_6H_5\\COOH\end{matrix}\rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$$

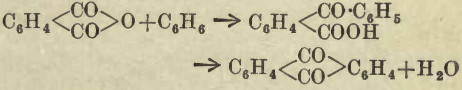
Simonis and Arand (Ber. 1909, 42, 3721) have succeeded in obtaining acyl benzoic acids by the interaction of Grignard reagents and phthalic acid itself, in addition to the dialkyl phthalides just described, *e.g.* using excess of magnesium ethyl bromide he isolated *o*-carboxy-phenyl ethyl ketone, m.p. 97°, $C_6H_4<\begin{matrix}COC_2H_5\\COOH\end{matrix}$.

Phthalic anhydride condenses with the cresols or their methyl ethers in presence of boric acid or aluminium chloride (*cf.* phthaleïn reaction with phenol):



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+C_6H_4(CH_3)OCH_3$$
$$\rightarrow C_6H_4<\begin{matrix}CO{\cdot}C_6H_3(CH_3)OCH_3\\COOH\end{matrix}$$
$$\rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2(CH_3)OCH_3.$$

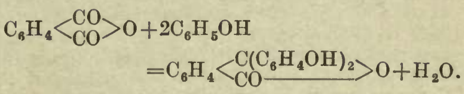
Sulphuric acid effects the closing of the ring in the condensation product, giving oxy-methyl anthraquinones and their methyl derivatives (*v.* METHYL ANTHRACENE; *cf.* Bentley, Gardner, and Weizmann, Chem. Soc. Trans. 1907, 91, 1626; Lambrecht, Ber. 1909, 42, 3591). The simplest case of the above condensation was worked out by Friedel and Crafts, who condensed phthalic anhydride and benzene in presence of aluminium chloride, with the ultimate formation of anthraquinone:—



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+C_6H_6\rightarrow C_6H_4<\begin{matrix}CO{\cdot}C_6H_5\\COOH\end{matrix}$$
$$\rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4+H_2O$$

(*V.* ANTHRAQUINONE, also Friedel and Crafts, Ann. Chim. Phys. [vi.] 14, 446; Heller, D. R. P. 193961.)

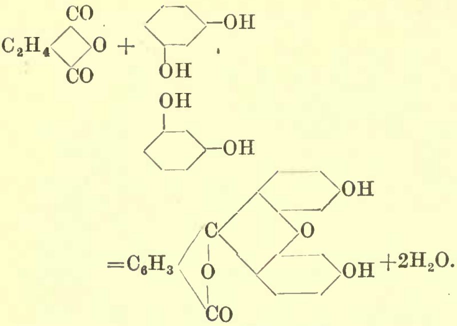
Phthalic anhydride condenses with phenols in presence of a dehydrating agent like zinc chloride or sulphuric acid, yielding a class of colouring matters known as the phthaleïns, which are fully dealt with in the article on TRIPHENYLMETHANE COLOURING MATTERS. The simplest member of the series is phenolphthaleïn, prepared by condensing phthalic anhydride with 2 molecules of pheno (Baeyer, Ber. 1874, 7, 968)—



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O+2C_6H_5OH$$
$$=C_6H_4<\begin{matrix}C(C_6H_4OH)_2\\CO\text{————}\end{matrix}>O+H_2O.$$

Phenolphthaleïn.

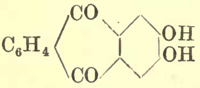
When resorcinol is substituted for phenol in this condensation, the product is the beautiful green fluorescein acid, the sodium salt of which is known in commerce as the dyestuff uranine—



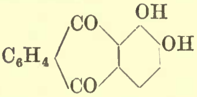
Fluorescein.

Eosin is another well-known member of this series of colouring matters, and is a bromo derivative of fluorescein.

Catechol condenses with phthalic anhydride in presence of concentrated sulphuric acid with formation of hystazarin and alizarin :

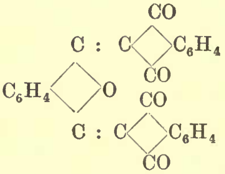


Hystazarin.

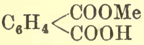


Alizarin.

An interesting condensation is that carried out by Marchese (Gaz. chim. ital. 37, ii. 303). Phthalic anhydride was caused to react with 2 molecules of sodium hydrindene carboxylic ester in presence of acetic anhydride, with the formation of the complex, anhydrophthalo-bisdiketohydrindene, m.p. about 325°—

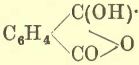


In many reactions phthalic anhydride shows a similarity to aldehydes. It is attacked by nitromethane in ether solution at 10°, and on adding methyl alcohol and sodium ethoxide, two products are isolated (Gabriel, Ber. 1903, 36, 570)—



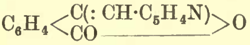
$$C_6H_4{<}\begin{matrix}COOMe\\ COOH\end{matrix}$$

and



$$C_6H_4{<}\begin{matrix}C(OH)\cdot CH_2\cdot NO_2\\ CO\end{matrix}{>}O$$

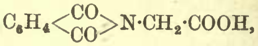
Again, phthalic anhydride condenses with 1 molecule of α-picolene just as does acetaldehyde or benzaldehyde, yielding in this case *γ-pyrophthalone*—



$$C_6H_4{<}\begin{matrix}C(:CH\cdot C_5H_4N)\\ CO\end{matrix}{>}O$$

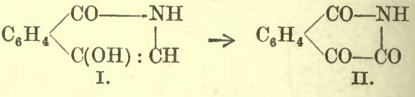
this being known as the 'phthalone reaction' (Düring, Ber. 1905, 38, 161). The same reaction occurs with quinaldine (Eibner, Ber. 1904, 37, 3605) with the lutidines, in some cases using zinc chloride (Scholze, Ber. 1905, 38, 2806: Langer, *ibid.* 3704), with α-methyl indol (Fischer, Annalen, 1887, 242, 381), and with cotarnine (Knoll and Co., D. R. P. 175079).

With *amines* and *amino acids*, phthalic anhydride gives an important series of compounds of the type, $C_6H_4{<}\begin{smallmatrix}CO\cdot NHR\\ COOH\end{smallmatrix}$ or the anhydride of this (*cf.* Tingle, J. Amer. Chem. Soc. 1910, 32, 113 and 1319). An example is that of glycine and phthalic anhydride, which give phthalyl glycine

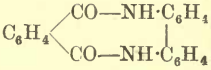


$$C_6H_4{<}\begin{matrix}CO\\ CO\end{matrix}{>}N\cdot CH_2\cdot COOH,$$

the ester of which Gabriel and Colman (Ber. 1902, 35, 2534) have converted into an *iso*-quinoline derivative on heating; hydrolysis of this leads to the compound (I.), which with nitric acid yields the interesting substance, phthalonimide (II.), m.p. 224°, a compound obtained also from carbindigo—

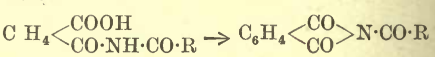


Andreasch has prepared in this way the phthalylalanine (m.p. 164°) (Monatsh. 25, 774; *cf.* also Fischer, Ber. 1907, 40, 489; and Annalen, 1888, 248, 152—for taurine). With benzidine the condensation is effected in aqueous solution, giving the compound—



(Koller, Ber. 1904, 37, 2880).

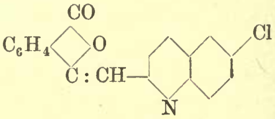
Sodium benzamide or sodium acetamide give the acyl phthalaminic acids (Titherley, Chem. Soc. Trans. 1906, 89, 708), which pass into the acyl phthalimides on dehydration with acetyl chloride—



$$C_6H_4{<}\begin{matrix}COOH\\ CO\cdot NH\cdot CO\cdot R\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CO\\ CO\end{matrix}{>}N\cdot CO\cdot R$$

Some applications of the above reactions to the preparation of dyestuffs are given :—

p-chlor-quinaldine condensed with phthalic anhydride and sulphonation of the quinophthalone so formed—

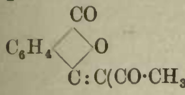


leads to a valuable yellow quinoline dyestuff (Bayer and Co., D. R. P. 204255; Eng. Pat. 1908, 28266; Frdl. 1908–1910, 280).

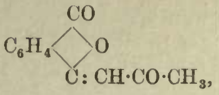
α-aminoanthraquinone in nitrobenzene condenses with phthalic anhydride in presence of phosphorus pentachloride yielding an orange-yellow dye (D. R. P. 216980; Eng. Pat. 27098, 1901; Frdl. 1908–1910, 753). Dyestuffs of the *acridine series* may be obtained by heating phthalic anhydride with phenylene or toluylene diamines in presence of the hydrochlorides of these bases, with or without a condensation agent such as zinc chloride (D. R. P. 141356; Eng. Pat. 11711, 1902; Frdl. 1902, 1904, 316).

Phthalyl chloride condenses with remarkable ease with substances possessing labile hydrogen atoms, which combine with the chlorine atoms causing the evolution of hydrogen chloride, *e.g.* malonic ester, acetoacetic ester, cyanacetic ester, &c.

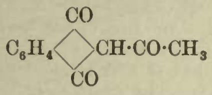
Bülow and his collaborators (Ber. 1904, 37, 4379; 1906, 39, 2275) have condensed it with acetyl acetone, and obtained the products—



and



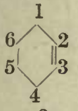
the second of which readily passes into β-acetyl diketo-hydrindene—



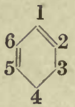
(*cf.* also Eibner, Ber. 1906, 39, 2202).

The Hydrophthalic Acids.

The classical work associated with the name of von Baeyer on the reduction of the phthalic acids has done much to extend our knowledge of valency, and especially of the constitution of the benzene ring. His researches (Annalen, 1873, 166, 346; 1890, 258, 214; 1892, 269, 154) enunciate the general rule, that entrance of hydrogen atoms into the molecule undergoing reduction, always takes place by attachment first to the α-carbon atoms, *i.e.* those which are adjacent to carboxyl groups. For example, adopting the special nomenclature for the hydrobenzenes, namely—

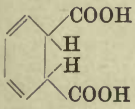


Δ^2



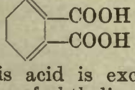
$\Delta^{1,5}$

then the reduction of ortho-phthalic acid with sodium amalgam in weak acetic acid solution, gave rise to the *trans-*$\Delta^{3,5}$*-dihydrophthalic acid*



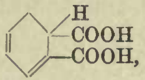
which melts at 210°. This is also prepared by electrolysis of phthalic acid in hot 15 p.c. aqueous sulphuric acid (Mettler, Ber, 1906, 39, 2941). The *cis*-form is only obtained by acting on this with acetic anhydride for 7 minutes, when the *cis-anhydride*, m.p. 100°, is formed, which on boiling with water yields the *cis-acid*, m.p. 175°; prolonged boiling converts the cis- into trans-form. The above $\Delta^{3,5}$ acid is what is known as a βγ doubly unsaturated acid, the double linkings being both attached to βγ carbon atoms with reference to the carboxyl groups. This type of acid readily undergoes inversion by digesting with alkalis such as caustic soda, due to the shifting of the double bonds to the αβ position in each case, so that the compound

$\Delta^{2,6}$*-dihydrophthalic acid*



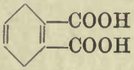
is obtained. This acid is exclusively formed when the reduction of phthalic acid with sodium amalgam is carried out in alkaline solution. It melts at 215°, and its anhydride, formed by the action of acetyl chloride, melts at 84°. Benzoic acid may be obtained from this $\Delta^{2,6}$-acid on oxidation. It is not affected by boiling with aqueous caustic soda, but very concentrated alcoholic potash produces the

$\Delta^{2,4}$*-Dihydrophthalic Acid*



which melts at 180°, and which is also obtained indirectly from the dihydrobromide of $\Delta^{2,6}$ dihydrophthalic acid and methyl alcoholic potash. When this $\Delta^{2,4}$-acid is boiled for 6 minutes with acetic anhydride, the anhydride of a new acid,

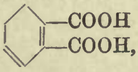
$\Delta^{1,4}$*-Dihydrophthalic Acid*



is formed, and on decomposing this with boiling water the above acid is obtained, m.p. 153°. Boiling caustic soda converts it into the $\Delta^{2,4}$ and $\Delta^{2,6}$ isomerides. It may be oxidised back again into phthalic acid. The anhydride of the acid melts at 133°.

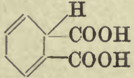
Abati and Bernardinis (Chem. Zentr. 1905, i. 1318) have isolated the two remaining dihydrophthalic acids by a careful scheme for separating the initial reduction products obtained as described by Baeyer. These are the—

$\Delta^{1,3}$*-Dihydrophthalic Acid*



the *anhydride* of which melts at 59°–60°, and also the

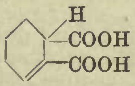
$\Delta^{2,5}$*-Dihydrophthalic Acid,*



which is obtained by heating the $\Delta^{1,3}$-acid to 230° in a closed tube; also by the intermediate shifting of the double linking in the $\Delta^{3,5}$-acid by means of caustic soda. Its *anhydride* melts at 73° (*cf.* also Abati, Gaz. chim. ital. 38, i. 152).

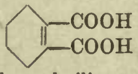
The *Tetrahydrides* are five in number. On reducing a boiling solution of sodium phthalate with sodium amalgam,

Δ^2*-Tetrahydrophthalic Acid*



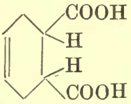
is formed, m.p. 215°; the anhydride melts at 79°, and is made by heating the acid. When this acid is heated for a considerable time at its melting-point, the anhydride of

Δ^1*-Tetrahydrophthalic Acid*

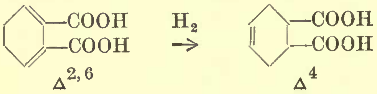


is produced, which on boiling with water gives rise to the above Δ^1-acid, m.p. 120°. The *anhydride* melts at 74°. This is also prepared by distilling the tetrahydride of pyromellitic acid. It changes back into the Δ^2-acid with concentrated potash, and permanganate oxidises it to adipic acid

Trans-Δ^4-tetrahydrophthalic Acid



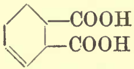
is formed, together with Δ^2-acid, by reducing the $\Delta^{2,6}$ dihydride in boiling water with sodium amalgam, that is—



(*Cf.* Thiele, Annalen, 1899, 306, 125.) This Δ^4-acid melts at 218°; its *anhydride*, made by the action of acetyl chloride, melts at 140°, and the *methyl ester* melts at 40°. The acid changes on heating into the *cis-form*, which is also obtained by reducing the $\Delta^{2,4}$-acid at 0° with sodium amalgam. This *cis*-Δ^4-acid melts at 174°, and its *anhydride* at 58°.

The remaining isomeride—

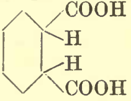
Δ^3-Tetrahydrophthalic Acid



is described by Abati and Vergari (Gazz. chim. ital. 1909, 39, ii. 142). Its *anhydride* melts at 70°–71°.

Both the di- and tetra-hydrophthalic acids are unstable towards permanganate and with milder oxidising agents may be oxidised back to phthalic acid. They form, as a rule, additive compounds with bromine or hydrobromic acid, and yield on reduction hexahydrophthalic acid (*cf.* also Graebe and Born, Annalen, 1867, 142, 330; Astie, Annalen, 258, 187). The physical properties of all these acids have been carefully measured by Abati and his collaborators (Gazz. chim. ital. 39, ii. 142; Chem. Zentr. 1907, i. 886).

Trans-hexahydrophthalic Acid



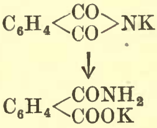
is prepared by reducing all the lower hydrides or their halogen additive compounds, either with sodium amalgam or zinc dust and acetic acid. It melts at 221°, and is not oxidised by cold permanganate. The *anhydride* melts at 140°, and the *dimethyl ester* at 33°. When slowly heated, the acid yields the anhydride of *cis-hexahydrophthalic acid*, from which the free acid is obtained by boiling with water. The acid melts at 192°, and the *anhydride* at 32°.

Nitrogen Derivatives.

Phthalimide $C_6H_4<\substack{CO\\CO}>NH$ is formed by the action of ammonia gas on molten phthalic anhydride, and is a most important stage in the manufacturing process of synthetic indigo. The method, due to Kuhara, is a quantitative one. Dry ammonia gas compressed in cylinders is used, and is passed into the phthalic anhydride until it ceases to be absorbed, the process occupying in all about 18 hours. The chief condition is that at the end of the operation, when complete transformation of anhydride into -imide has been effected, the mass should remain in the molten state; the anhydride melts at 128° and the imide at 228°, hence during the progress of the operation the temperature should be maintained 1° above the latter. The molten product is run off and allowed to cool and crystallised in open pans; 650 kilos. of anhydride yield 635 kilos. of phthalimide.

Phthalimide may also be prepared by heating phthalic anhydride with urea (Dunlap), or with aliphatic nitriles (Matthews, J. Amer. Chem. Soc. 1896, 18, 680; 1898, 20, 654), or with formamide, acetamide, and other amides, acetanilide, and similar compounds. It exists as colourless plates, m.p. 228°, and may be sublimed.

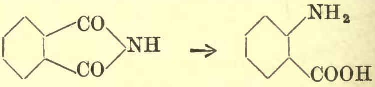
Reactions.—Amyl alcohol and sodium reduce *phthalimide* to *o*-methyl benzylamine (Bamberger, Ber. 1888, 21, 1888). Distilled with lime, it loses water and carbon dioxide, yielding benzonitrile (Reese, Annalen, 1887, 242, 5). With alcoholic potash it forms a potassium derivative,



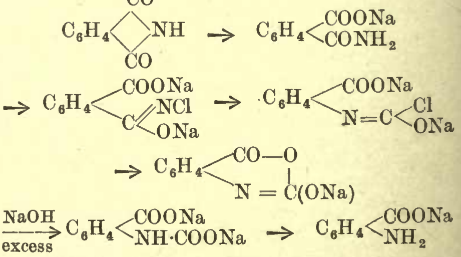
$$\begin{array}{c} C_6H_4<\substack{CO\\CO}>NK \\ \downarrow \\ C_6H_4<\substack{CONH_2\\COOK} \end{array}$$

which on boiling with water is converted into potassium phthalamate.

From the point of view of indigo its most important reaction is that discovered by Hoogewerff and van Dorp (D. R. P. 55988), with alkaline KOBr at 80°, when it is transformed into *o*-aminobenzoic acid, or anthranilic acid—



Mohr (J. pr. Chem. [ii.] 80, 1; D. R. PP. 127138, 139218; Frdl. 1902–1904, 118–120) has modified this by using NaOCl, and states that sodium isatoic acid anhydride is probably formed as an intermediate compound, which excess of caustic soda converts into sodium anthranilate—



$$C_6H_4\left\langle\substack{CO\\ \\ CO}\right\rangle NH \rightarrow C_6H_4<\substack{COONa\\CONH_2}$$

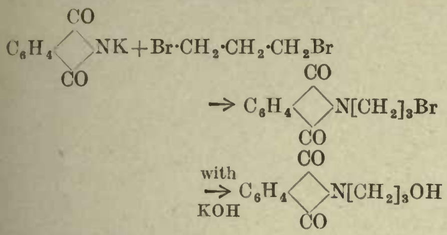
$$\rightarrow C_6H_4<\substack{COONa\\C<\substack{=NCl\\ONa}} \rightarrow C_6H_4<\substack{COONa\\N=C<\substack{Cl\\ONa}}$$

$$\rightarrow C_6H_4<\substack{CO-O\\ \quad\ \ | \\ N=C(ONa)}$$

$$\xrightarrow[\text{excess}]{\text{NaOH}} C_6H_4<\substack{COONa\\NH\cdot COONa} \rightarrow C_6H_4<\substack{COONa\\NH_2}$$

Phthalimide forms a potassium derivative exactly as does malonic ester, in which also the metallic radicle may be substituted for alkyl by contact with halogen compounds (*see resumé* by Sörensen, Zeitsch. physikal Chem. 44, 448; Chem. Zentr. 1905, ii. 401; *cf.* also Bull.

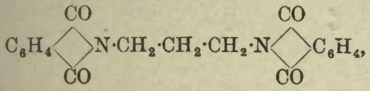
Soc. chim. 33, 1042). Gabriel describes an interesting example of this use of potassium phthalimide with dibromopropane—



$$C_6H_4<^{CO}_{CO}>NK + Br\cdot CH_2\cdot CH_2\cdot CH_2Br \rightarrow C_6H_4<^{CO}_{CO}>N[CH_2]_3Br \xrightarrow[KOH]{with} C_6H_4<^{CO}_{CO}>N[CH_2]_3OH$$

(Ber. 1905, 38, 2389).

Two molecules of phthalimide may also combine with the halogen derivative, giving



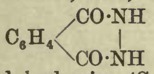
$$C_6H_4<^{CO}_{CO}>N\cdot CH_2\cdot CH_2\cdot CH_2\cdot N<^{CO}_{CO}>C_6H_4,$$

and this on hydrolysis with mineral acids yields trimethylene diamine and 2 molecules of phthalic acid, thus providing an excellent general method for the preparation of diamines.

Various mercaptan derivatives of phthalimide have been prepared by Manasse (Ber. 1902, 35, 1367).

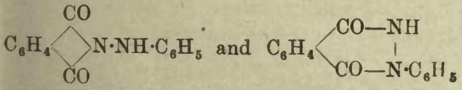
The German patent No. 139553 describes the preparation of *phthal-chlorimide* by leading chlorine into an aqueous suspension of phthalimide.

A 40 p.c. solution of formaldehyde gives with phthalimide a methyl phthalimide of m.p. 132° (Breslauer and Pictet, Ber. 1907, 40, 3784). Various Grignard reagents have been tried with success upon phthalimide (*cf.* Béis, Compt. rend. 138, 987; Sachs and Ludwig, Ber. 1904, 37, 385). With tin and hydrochloric acid it is reduced to phthalimidine $C_6H_4<^{CH_2}_{CO}>NH$ (Graebe, Ber. 1884, 17, 2598; Annalen, 1888, 247291).

Phthalyl hydrazide  $C_6H_4<^{CO\cdot NH}_{CO\cdot NH}$ is made from the anhydride and hydrazine (Curtius, J. pr. Chem. [ii.] 51, 376). The phenyl hydrazine derivatives exists in two forms; the first product of the condensation is probably a simple additive compound—

$$C_6H_4<^{COOH}_{CONH\cdot NH\cdot C_6H_5},$$

which splits off water in two ways, giving—



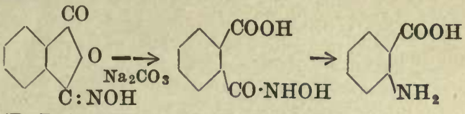
$$C_6H_4<^{CO}_{CO}>N\cdot NH\cdot C_6H_5 \quad \text{and} \quad C_6H_4<^{CO—NH}_{CO—N\cdot C_6H_5}$$

α Phthalyl phenylhydrazine, m.p. 179°. β form.

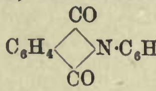
(Dunlap, J. Amer. Chem. Soc. 1905, 27, 1091).

Phthalyl semicarbazide melts at 262°.

Phthalylhydroxylamine. Hydroxylamine condenses with phthalic anhydride in aqueous dilute alcoholic solution or in caustic soda, with formation of phthalylhydroxylamine, m.p. 204°–206° in good yields (Basler Chemische Fabrik, D. R. PP. 130680, 130681). Treatment of the hydrochloride of this with sodium carbonate, and subsequent action of caustic soda, leads to the formation of anthranilic acid—



(D. R. P. 136788; Frdl. 1902–1904, 117).

Phthalanil  $C_6H_4<^{CO}_{CO}>N\cdot C_6H_5$, m.p 205°, is formed by heating 1 molecule of sodium phthalate and 2 molecules of aniline hydrochloride in a closed tube for 6 hours at 200° (J. Amer. Chem. Soc. 1903, 25, 612).

Phthalonitrile $C_6H_4<^{CN}_{CN}$ is obtained from 2-aminobenzonitrile by conversion of the NH_2 group into CN (Pinnow and Sämann, Ber. 1896, 29, 630); and from *o*-cyanobenzaldoxim by dehydration in contact with acetic anhydride (Posner, Ber. 1897, 30, 1698). It forms odourless needles, m.p. 142°, distils without decomposition, and is volatile in steam. It is transformed into phthalic acid on hydrolysis with concentrated hydrochloric acid.

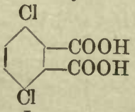
Seminitrile of Phthalic acid $C_6H_4<^{CN}_{COOH}$ (*o*-cyanobenzoic acid) is prepared from anthranilic acid by the Sandmeyer reaction (Ber. 1885, 18, 1499); by the action of NH_3 upon phthalyl chloride (Hoogewerff and van Dorp, Rec. trav. chim. 11, 91; *cf.* Kuhara, Amer. Chem. J. 3, 26; Auger, Ann. Chim. Phys. [vi.] 22, 289); and from benzaldehydeoxime-carboxylic acid by contact with acetic anhydride. It exists as needles melting at 180°–190° and changing simultaneously into phthalimide. Heating with water produces acid ammonium phthalate. The *methyl ester* melts at 51°, and the *ethyl ester* at 70°.

SUBSTITUTED PHTHALIC ACIDS.

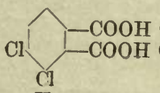
Many *chloro, bromo, nitro, sulpho* substituted phthalic acids are known, and references to these are frequent in Beilstein's Handbuch der Organischen Chemie, vol. ii. and its supplement; also Frdl. 1887–1890, 93; Villiger, Ber. 1909, 42, 3529. When phthalic anhydride, dissolved in fuming sulphuric acid, is treated with chlorine in presence of a little iodine (Juvalta, D. R. P. 50177), the following reaction occurs:—

$$C_6H_4<^{CO}_{CO}>O + 4Cl + 2SO_3$$
$$= Cl_2\cdot C_6H_2<^{CO}_{CO}>O + 2\ Cl\cdot SO_3H$$

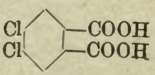
Separation of the products is possible owing to a difference in solubility of the zinc salts, by a recrystallisation of which three isomerides are separated. The chief product is 3 : 6-*dichloro*) *phthalic acid* (I.). smaller quantities of 3 : 4 (II.- and very little of 4 : 5 (III.), being isolated—



I.



II.

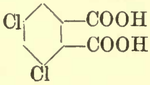


III.

The 3 : 6 acid has m.p. 253°–258°; and its anhydride, m.p. 339°.

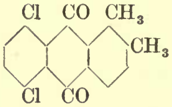
These acids are more soluble in water and ether than ordinary phthalic acid, and the anhydrides can be distilled (*cf.* also Graebe, Ber. 1900, 33, 2019).

A fourth isomeride is described by Crossley and Le Sueur (Chem. Soc. Trans. 1906, 81, 1533), viz. the 3 : 5-*dichlorophthalic acid*



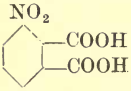
(*cf.* also Claus, Ber. 18, 1370; 19, 3175; J. pr. Chem. [ii.] 43, 253, 582; Le Royer, Annalen, 1887, 238, 350).

3 : 6-*dichlorophthalic anhydride*, which is now a commercial product, has been condensed with the three xylenes and the closing of the ring effected, with formation of dichloro-dimethyl-anthraquinones (Harrop, Norris and Weizmann, Chem. Soc. Trans. 1909, 95, 1312)—

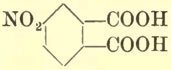


Of the four possible *dibromophthalic acids* only the *para* (3 : 6-), m.p. 135°, is at present made, the yield being 30 p.c.; 100 grams of dibromonaphthalene is strongly heated for 2 hours with 2 litres of nitric acid (sp.gr. 1·4); first a nitrated product is obtained, and then on evaporation of the mother liquors to one-third the volume, white crystals of the 3 : 6-*dibromophthalic acid* appear (Severin, Chem. Zentr. 1907, i. 1119).

Nitro-phthalic acid. Holleman (Chem. Zentr. 1908, ii. 2011) has studied quantitatively the action of concentrated nitric acid on phthalic acid at 30°, and has found that the product contains 49·5 p.c. of the α- and 50·5 p.c. of the *β-nitrophthalic acid*—



α.

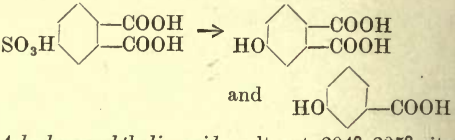


β.

Sulpho-phthalic acids. The Badische Anilin und Soda Fabrik, has obtained an English patent (J. Y. Johnson, No. 18221, August 17, 1896) for the preparation of a disulphonic acid. 100 kilos. of naphthalene is dissolved in 300 kilos. of fuming sulphuric acid (23 p.c. SO_3) and mixed with 1200 kilos. concentrated sulphuric acid (95 p.c.). The mass is heated for 10 hours at about 250°; a certain amount of phthalic acid distils over during the reaction. The product is neutralised with calcium or barium carbonate and worked up in the usual way. The new *disulphonic acid* of phthalic acid may be separated from water in crystalline nodules in the form of its barium salt.

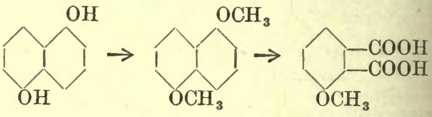
If the temperature is maintained at about 220°, a *monosulphonate* of phthalic acid is obtained.

Hydroxy-phthalic acids. Bentley and Weizmann (Chem. Soc. Trans. 1907, 91, 98) have sulphonated phthalic anhydride with fuming sulphuric acid (73 p.c. SO_3) at 200° and fused the products with caustic soda, obtaining in this way 4-*hydroxy-phthalic acid*, and as by-product *m*-hydroxybenzoic acid—

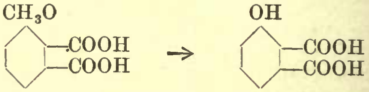


4-*hydroxy-phthalic acid* melts at 204°–205°, its anhydride at 171°–173°; the *methoxy acid* at 178° and the anhydride of this at 98°.

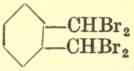
The same authors, with Miss Rona Robinson (Chem. Soc. Trans. 1907, 91, 104), prepared 1 : 5-*di-methoxy-naphthalene* and oxidised this with permanganate, obtaining 3-*methoxy-phthalic acid*, m.p. 173°, the *anhydride* of which melts at 160°—



Fusion of the methoxy acid with caustic potash gives rise to the 3-*hydroxy-phthalic acid*, m.p. 150°—

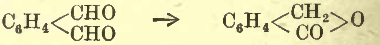


Phthalaldehyde $C_6H_4<\substack{CHO \\ CHO}$. When *o*-xylene is brominated it yields the tetrabromide



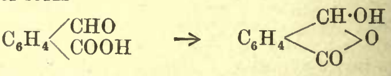
If 400 grams of this bromide are heated with 360 grams of finely powdered crystalline potassium oxalate in an oil-bath for 40 hours, in contact with 2½ litres of water and 2½ litres of 95 p.c. ethyl alcohol, a clear yellow solution results, with evolution of some carbon monoxide and dioxide. After distilling off 2 litres of alcohol, which is used again subsequently, 700 grams of crystalline sodium phosphate are added, and the mass is subjected to distillation in steam, which drives over the phthalic aldehyde. The product is readily soluble in water, and therefore the distillate is extracted several times with acetic ester, which dissolves out the aldehyde, a 90 p.c. yield being obtained in the form of yellow needles, m.p. 56° (Thiele and Günther, Annalen, 1906, 347, 106).

Strong alkali converts phthalaldehyde into phthalide, which appears to be an intramolecular change into a more stable isomeride—



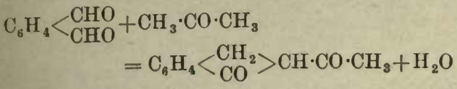
$$C_6H_4<\substack{CHO \\ CHO} \rightarrow C_6H_4<\substack{CH_2 \\ CO}>O$$

It is interesting to compare this with the 'lactone tautomerism' of aldehydo phthalic acid and hydroxy phthalide, which can react in either form—



$$C_6H_4<\substack{CHO \\ COOH} \rightarrow C_6H_4<\substack{CH{\cdot}OH \\ CO}>O$$

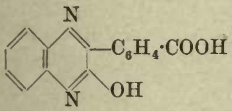
Phthalaldehyde condenses readily with a large number of substances by virtue of its two —CHO groupings; *e.g.* with acetone it yields β-acetyl hydrindone (Thiele and Falk, Annalen. 1906, 347, 112; 1909, 369, 287)—



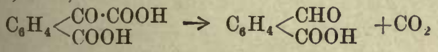
$$C_6H_4<\begin{matrix}CHO\\CHO\end{matrix}+CH_3{\cdot}CO{\cdot}CH_3 = C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH{\cdot}CO{\cdot}CH_3+H_2O$$

Phthalonic acid $C_6H_4<\begin{matrix}COOH\\CO{\cdot}COOH\end{matrix}$, m.p. 144°–145°, is formed at an intermediate stage of the oxidation of naphthalene to phthalic acid, especially when the reagent used is permanganate (Annalen, 1887, 240, 142; Daly, J. Phys. Chem. 11, 93). It is also produced by the action of nitric acid on tetrachlor-ketohydrindene (Zinke and Fries, Annalen, 1904, 334, 342). Its *acid methyl ester* melts at 79°–81°, and its neutral *methyl ester* at 66°–68° (*cf.* Frdl. 1894–1897, 162–163; D. R. PP. 79693, 86914 (Tcherniac)).

Phthalonic acid takes part in numerous reactions, principally those involving the keto group: *e.g.* it condenses with *o*-phenylene diamin (Gazz. chim. ital. 1904, 34, i. 493), giving the compound—



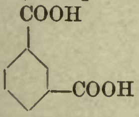
A warm sodium bisulphite solution of sodium phthalonate gives on evaporation and subsequent treatment with hydrochloric acid, *aldehydo-phthalic acid* (Wegscheider and Bondi, Monatsh. 26, 1039)



$$C_6H_4<\begin{matrix}CO{\cdot}COOH\\COOH\end{matrix} \rightarrow C_6H_4<\begin{matrix}CHO\\COOH\end{matrix} + CO_2$$

The following is the best method of preparing phthalonic acid: 10 grams naphthalene is dissolved in 1 litre of water and 90 grams pure $KMnO_4$, or its equivalent of the commercial permanganate, is added, and the whole boiled until the solution is completely decolourised. The removal of the excess of naphthalene (2·5 grams) is effected by steam distillation, the oxide of manganese is filtered off, and the filtrate evaporated and then acidified and the product extracted or allowed to crystallise. The yield is 9 grams of phthalonic acid and 1 gram of phthalic acid.

***iso*Phthalic acid** (meta-phthalic acid)



is prepared by the oxidation of *m*-xylene with permanganate (Nölting, Ber. 1885, 18, 2687) or with chromic acid (Fitting and Velguth, Annalen, 1868, 148, 11; 1870, 153, 268); or by converting *m*-xylene into the dibromide by bromination at 125°, treating this with hot alcoholic potash, and oxidising the resulting ether with chromic acid mixture (Kipping, Ber. 1888, 21, 46). It is also obtained by fusing potassium formate with potassium benzoate (Richter, Ber. 1873, 6, 876), or with potassium *m*-brombenzoate (Ador and Meyer, Annalen, 1871, 159, 16), or with benzene disulphonic acid (Barth and Senhofer, Annalen, 1871, 159, 228); and by the action of a hot solution of cuprous potassium cyanide on *m*-diazobenzoic chloride and saponification of the resulting nitrile (Sandmeyer, Ber. 1885, 18, 1498).

It exists in the form of long slender needles when crystallised from water, which melt at about 300° and which may be sublimed, without, however, forming the corresponding anhydride.

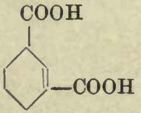
The *dimethyl ester* melts at 67°–68° (Baeyer, Ber. 1898. 31, 1404), and the *diethyl ester* at 11·5° (*cf.* Perkin, Chem. Soc. Trans. 1896, 69, 1238, for physical properties).

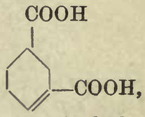
It forms a *hydrazide*, m.p. 220°, by heating with hydrazine hydrate in absolute alcohol (Davids, J. pr. Chem. [ii.] 54, 74), and also an *azide*, $C_6H_4(CON_3)_2$.

Hydro-isophthalic Acids.

These acids are chiefly due to the work of Perkin and Pickles (Chem. Soc. Trans. 1905, 87, 293) and Perkin and Goodwin (*ibid.* 843).

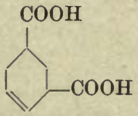
The *dihydro-isophthalic acids* are not well known. The $\Delta^{1,4}$-acid, m.p. 270°, has been obtained from 1:3-dibromo-trans-hexahydro-*iso*phthalic acid by the agency of potash; and the $\Delta^{2,4}$*-dihydro-acid*, m.p. 255°, is also described as obtained in a similar manner from the 3:4-dibromohexahydro acid, but the constitution of these two acids is still regarded as unsettled.

All the four possible *tetrahydro acids* have been isolated. *iso*-Phthalic acid on reduction with sodium amalgam yields two acids, Δ^2 and the cis-form of Δ^4. Δ^2*-Tetrahydro-isophthalic acid*  melts at 168°, is very soluble in water, and its anhydride melts at 78°. By the agency of caustic potash or hydrochloric acid it yields the sparingly soluble Δ^3*-tetrahydroisophthalic acid*



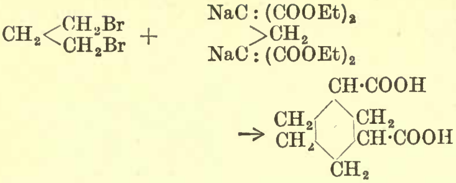
m.p. 244°, which gives, with acetic anhydride, the anhydride of Δ^2-acid, m.p. 78°.

Cis-Δ^4*-tetrahydroisophthalic acid*



is isolated from the original reduction product, as stated above. It melts at 165°, is very soluble in water, and is easily converted into the *trans-acid* with concentrated hydrochloric acid. This trans-form is sparingly soluble, and melts at 227°.

Cis- and *trans-hexahydroisophthalic acids*, m.p. 163° and 148° respectively, were obtained synthetically by Perkin and Prentice (Chem. Soc. Trans. 1891, 59, 808; *cf.*, however, Perkin and Goodwin, Chem. Soc. Trans. 1905, 87, 843), who condensed trimethylene bromide with sodio-methylene-malonic ester—



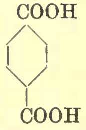
The tetrabasic ester first formed yielded on hydrolysis a mixture of cis- and trans-hexahydro-*iso*phthalic acids. Bayer and Villiger were able to verify these results by the actual reduction of *iso*phthalic acid (Annalen, 1893, 276, 255).

5-Chloro-*iso*phthalic acid is prepared by the oxidation of 5-chloro-*m*-toluic acid with alkaline permanganate (Klages, Knoevenagel, Ber. 1895, 28, 2045); and *tetra-chlor* and *tetra-brom* derivatives are prepared by oxidation of the correspondingly substituted xylenes (Rupp, Ber. 1896, 29, 1631).

2-Nitro- and **4-nitro-*iso*phthalic** acids have been prepared by Holleman (Rec. trav. chim. 27, 260; Chem. Zentr. 1908, ii. 2011) by oxidising the corresponding nitro-*m*-xylenes with alkaline permanganate. Direct nitration of *iso*phthalic acid with concentrated nitric acid at 30° was found to give 97 p.c. 5-nitro- and 3 p.c. 4-nitro*iso*Phthalic acids. The 2-nitro- and 4-nitro*iso*Phthalic acids melt at 300° and 245° respectively.

***iso*Phthalic aldehyde** is prepared in theoretical yields from ω-tetrabromo-*m*-xylene by boiling with potassium oxalate in aqueous alcohol. It melts at 89·5° and exists as colourless silky needles. The dioxide melts at 180° (Thiele and Günther, Annalen, 1906, 347, 109).

Terephthalic acid (*para*-phthalic acid)—



is formed by the oxidation of most derivatives of benzene having carbon chains in the *para* position, *e.g.* the terpenes, *para*-xylene, *p*-toluic acid, &c., and by the analogous methods given under *iso*Phthalic acid, such as the fusion of *p*-disulphobenzene with sodium formate (Remsen, Ber. 1872, 5, 379). It may be prepared by Baeyer's method (Annalen, 1888, 245, 139), from dibromo-*p*-xylene, $C_6H_4(CH_2Br)_2$, by digestion with potassium acetate in absolute alcohol, and subsequent oxidation of the acetate, $C_6H_4(CH_2O{\cdot}OCCH_3)_2$ with alkaline permanganate; or by the method of Beilstein (Annalen, 1865, 133, 41), in which *p*-xylene is oxidised with chromic acid mixture.

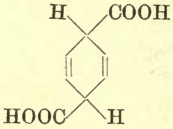
Terephthalic acid is a white crystalline powder, which sublimes without melting; its *dimethyl* ester melts at 140°. The acid is very sparingly soluble in water, alcohol, acetic acid, ether, or chloroform. When heated with lime it yields benzene. Phthalic acid precipitates terephthalic acid from its salts in solution.

Terephthalic acid in the form of its chloride has been condensed with α-amino-anthraquinone in nitrobenzene solution, and is said to produce a yellow dye (D. R. P. 216980; Eng. Pat. 27098; Frdl. 1908–1910, 753).

Hydro-terephthalic Acids.

By reducing terephthalic acid with sodium amalgam in aqueous solution through which a stream of carbon dioxide was passed, Baeyer (Annalen, 1888, 245, 142; 1889, 251, 257; 1892, 269, 148) was able to show that two atoms of hydrogen attach themselves to the α-carbon atoms in the molecule.

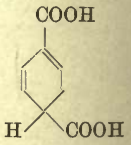
Trans-$\Delta^{2,5}$-dihydroterephthalic acid



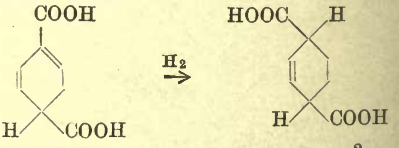
crystallises out first from the acidified product, and may be characterised by its methyl ester, m.p. 77°; the acid seems to have no definite melting-point.

The *cis*-$\Delta^{2,5}$-acid is extracted from the mother liquors by means of ether; its salts are more soluble than those of the trans-form. The *trans*-form may also be prepared by electrolysis of a warm alcoholic solution of terephthalic acid containing aqueous sulphuric acid (Mettler, Ber. 1906, 39, 2933). Alkaline permanganate reconverts it into terephthalic acid. As the double linkings are both situated in βγ positions, inversion into acids containing αβ- double linkings is readily effected. This takes place in two stages, giving the $\Delta^{1,5}$ and $\Delta^{1,4}$ acids—

$\Delta^{1,5}$*-dihydroterephthalic acid*

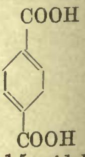


is obtained by boiling the above $\Delta^{2,5}$-acid with water, and may therefore be prepared directly from terephthalic acid by reduction in hot solution. Its *methyl ester* melts at 40°. Further treatment with sodium amalgam produces the Δ^2 *-tetrahydro* acid, following the rule that it is only αβ double-bonds which undergo reduction under these conditions—

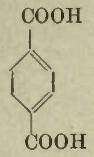


$\Delta^{1,5}$ Δ^2

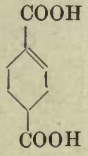
$\Delta^{1,4}$*-dihydroterephthalic acid*



is obtained from either the $\Delta^{2,5}$- or $\Delta^{1,5}$-acid by warming with caustic soda, both double bonds being now in αβ positions. It is therefore readily prepared by reducing terephthalic acid with sodium amalgam in alkaline solution. The *methyl ester* melts at 130°.

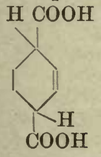


$\Delta^{1,3}$-*dihydroterephthalic acid* is prepared indirectly from the dibromide of Δ^2-tetrahydroterephthalic acid by the action of methyl alcoholic potash. Its *methyl ester* melts at 85°. In accordance with Thiele's view of the reduction of conjugated double linkings, it reduces to Δ^2-tetrahydroterephthalic acid.



Δ^1-*Tetrahydroterephthalic acid* is prepared by boiling 1 part of terephthalic acid in caustic soda for 40 hours, and gradually adding 100 parts of sodium amalgam (4 p.c.). It melts above 300°; the *methyl ester* melts at 39° (Baeyer, Ber. 1886, 19, 1805; Annalen, 1888, 245, 160; 1890, 258, 32).

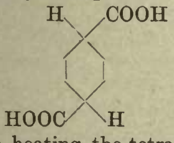
Trans-Δ^2-tetrahydroterephthalic acid



melts about 220°, and is obtained from the $\Delta^{1,5}$-dihydro acid or from the dibromo-$\Delta^{1,3}$-acid by reduction. The *methyl ester* melts at 3°.

Cis-Δ^2 tetrahydroterephthalic acid is formed together with the trans-form by reducing the $\Delta^{1,4}$-dihydro-acid with sodium amalgam in the cold.

Trans-hexahydroterephthalic acid



is formed on heating the tetrahydro acids with aqueous hydriodic acid at 240°. It melts at 300°; its *methyl ester* melts at 71° (Baeyer, Ber. 1886, 19, 1806; Annalen, 1888, 245, 170; 1889, 251, 257). Its synthesis has been accomplished by Mackenzie and Perkin (Chem. Soc. Trans. 1892, 61, 174).

The *cis-* form, m.p. 162°, is obtained by reducing the very soluble bromo-hexahydroterephthalic acid with zinc dust and acetic acid. Its methyl ester does not crystallise.

2 : 5-dichloroterephthalic acid has been prepared by Bocchi (Gazz. chim. ital. 26, ii. 406) from the dichlorocymene by oxidation with nitric acid.

Terephthalic aldehyde is prepared exactly as described in the case of phthalic aldehyde (Annalen. 1906, 347, 110). It exists as long needles, m.p. 116°.

PHTHALIC ANHYDRIDE *v.* PHTHALIC ACID.

PHTHALIDE *v.* LACTONES.

PHYCITE. Identical with erythrol (*q.v.*).

PHYSOSTIGMINE *v.* ORDEAL BEAN; also VEGETO ALKALOIDS.

PHYTIN, *inositol phosphoric acid*

$$C_6H_6(PO_4H_2)_6,$$

occurs in many plant seeds, usually as the calcium-magnesium salt. In bran, in the seeds of red-fir, peas, beans, pumpkin, red and yellow lupin, and in the potato and other tubers and bulbs, the greater part of the phosphorus exists in this form (Patten and Hart, Amer. Chem. J. 1904, 31, 564).

It occurs to the extent of 2 p.c. in wheat bran and 8 p.c in rice-bran (Suzuki and others, Bull. Coll. Agric. Tokyo. 1907, 7, 495), and is prepared from the latter by extraction with 0·2 p.c. hydrochloric acid. It is purified by precipitating with magnesia, washing the preparation, dissolving in acid and decolourising with charcoal, and again precipitating with magnesia (Contardi, Atti. R. Accad. Lincei. 1909, [v.] 18, i. 64). It is soluble in water and dilute alcohol; insoluble in benzene, ether, &c.; it does not crystallise (Posternak, Compt. rend. 1903, 137, 337 and 439). In plants it is associated with an enzyme, *phytase*, by which it is hydrolysed into inositol and phosphoric acid; this hydrolysis can also be brought about by dilute acids or by 20 p.c. caustic soda at 220° (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118; *see* also Neuberg, Biochem. Zeitsch. 1908, 9, 557; Levene, *ibid.* 1909, 16, 399; Neuberg, *ibid.* 1909, 16, 406).

The solution of the pure acid is stable and, when administered to animals by the mouth, has no ill effects (Mendel and Underhill, Amer. J. Physiol. 1906, 17, 75); 35 p.c. is absorbed by the organism, the remainder being eliminated as inorganic phosphates (Horner, Biochem. Zeit. 2, 428).

PHYTOSTEROL (phytosterin)

$$C_{26}H_{44}O,H_2O, \text{ or } C_{27}H_{46}O$$

is vegetable cholesterin (Hesse, Annalen, 1872, 192, 175). It is contained in calabar beans, in the bark of *Hamamelis virginiana* (Linn.) (Grüttner, Arch. Pharm. 1898, 236, 278); in the bark of *Berberis*; in *Ergot*, in the leaves of *Eriodictyon crassifolium* (Benth.) (Power and Tutin, Pharm. Rev. 1906 24, 300); in prunas bark (Finnemore, Pharm. J. 1910, [iv.] 31, 604); in the dried rhizome and roots of the yellow jasmine (Moore, Chem. Soc. Trans. 1910, 2226), and of the *Cimcifuga racemosa* (Nutt.) (Finnemore, Pharm. J. 1910, [iv.] 31, 142); in the lichen, *Endocarpon miniatum* (L.) Ach. (Hesse, J. pr. Chem. 1898, [ii.] 58, 465); in wheat germs, in the wild cherry bark, in rape oil, in cocoanut, cottonseed, and in nearly all vegetable oils, and in various lamp oils (Marcusson, J. Soc. Chem. Ind. 1901, 484). It has also been found, probably in the form of esters, in certain peaty soils (Schreiner and Shorez, Chem. News, 1912, 105, 40). *See* also Kerstein (Chem. Zentr. 1899, ii. 91); Mügge (Zeitschr. Nahr. Genuss. 1898, 1, 45); Schmidt and Kerstein (Arch. Pharm. [iii.] 28, 49); Matthes and Rohdich (Ber. 1908, 41, 19, 1591); Matthes and Ackermann (*ibid.* 2000); Cohen (Arch. Pharm. 1908, 246, 515, 592); Powers and Rogerson (Pharm. J. 1909, iv. 29, 7; *ibid.* 1910, [iv.] 30, 326); Sani (Chem. Zentr. 1903, i. 93); Tarbouriech and Hardy (*ibid.* 1907, ii. 969); Sanders (Arch. Pharm. 1908, 246, 165); Matthes and Heintz (*ibid.* 1909, 247, 161); Klobb (Compt. rend. 1909, 149, 999); Power and Moore (Chem. Soc. Trans. 1909, 246, 1987); Dorée (*ibid.* 649); Rogerson (*ibid.* 1910, 1012); Menozzi and Moreschi (Chem. Zentr. 1910, i. 1777).

Extraction. The seeds, bark, or leaves are treated with ligroin, the solution is then evaporated, the residue dried between filter paper and crystallised from alcohol. From oils and fats phytosterol is obtained by saponification with alcoholic alkali and subsequent extraction with ether (Raumer, Zeitsch. angew. Chem. 1898, 24, 555; Wolf, Chem. Zeit. 1898, 22, 805; Heiduschka and Gloth, Pharm. Zentr.-h. 1909, 50 333). Phytosterol crystallises in needles and in plates, is soluble in chloroform, but insoluble in water and in alkalis and gives the same reaction as cholesterol with chloroform and sulphuric acid. It has m.p. 132°–136°, but this, as well as its constitution, varies with the source from which it is obtained.

Windaus and Hauth have resolved the crude phytosterol of calabar beans into two constituents: (1) *stigmasterol* or *β-phytosterol*, $C_{30}H_{50}O,H_2O$ or $C_{30}H_{48}O,H_2O$, m.p. 170°; $[\alpha]_D$–45·01° at 21° in $CHCl_3$, which gives a sparingly soluble *bromide* and an *acetate*, m.p. 141°, and a *tetra-bromo-acetate* decomposing at 211°–212°.

(2) *Sitosterol* or *α-phytosterol*, $C_{27}H_{46}O$ or $C_{27}H_{44}O$, m.p. 136°–137° $[\alpha]_D$-34·4° in chloroform, which is identical with the phytosterol contained in wheat germs (Burian, Monatsh. 1897, 18, 551). It yields a readily soluble bromide, and when reduced with sodium and alcohol forms *dihydrophytosterol*, $C_{27}H_{48}O$, m.p. 175°, the dichloride of which on reduction yields *dihydrophytostene*, $C_{27}H_{48}$, m.p. 80°–81°. It is probable that most of the phytosterols of m.p. about 135° consist entirely or chiefly of sitosterol (Ber. 1906, 39, 4378; *ibid.* 1907, 40, 3681; Pickard and Yates, Chem. Soc. Trans. 1908, 1929; Windaus and Welsch, Ber. 1909, 42, 612). According to Thoms (Arch. Pharm. 1897, 235, 39), the term phytosterol should be given to all unsaturated alcohols of high molecular weight, which give the characteristic cholesterol colour reactions and which owe their origin to physiological processes similar to those producing cholesterol.

Phytosterol esters may be obtained by heating the alcohol with 5 times its weight of the required acid or anhydride in a sealed tube on the water bath. The melting-points of some of the esters differ with the source of the phytosterol, but in all cases they are considerably higher than the corresponding cholesterol esters, and this can be used as one method of distinguishing between the two alcohols (Bömer and Winter, Zeitsch. Nahr. Genussm. 1901, 4, 865; Jaeger, Rec. trav. chim. 1907, 26, 311; Menozzi and Moreschi, *l.c.*); for other methods compare Kreis (Chem. Zeit. 1899, 23, 21); Ottolenghi (Atti. R. Accad. Lincei, 1906, [v.] 15, i. 44); Jaeger (Rec. trav. chim. 1906, 25, 334). The separation of phytosterol from cholesterol is based on the difference of the solubility of their dibromides in a mixture of ether and glacial acetic acid (Windaus, Chem. Zeit. 1906, 30, 1011). For the detection and estimation of phytosterol in fats, *see* Kreis and Wolf, Chem. Zeit. 1898, 22, 805; Foerster, *ibid.* 1899, 23, 188; Wirthle, *ibid.* 250; Kreis and Rudin, *ibid.* 986; Juckenack and Hilger, Arch. Pharm. 1898, 236, 367; Ritter, Chem. Zeit. 1901, 25, 872; *ibid.* 1902, 26, Rep. 100.

For other literature on phytosterol, compare Power and Tutin (Chem. Soc. Trans. 1908, 909); Molinari and Fenaroli (Ber. 1908, 41, 2785); Heiduschka and Gloth (Chem. Zentr. 1908, ii. 1519).

PICAMAR $C_{10}H_{14}O_3$ is easily obtained from wood tar; preferably from birch tar, which contains it in largest quantity. It is isolated by means of its potassium compound, which is purified by recrystallisation and decomposed by an acid; is a colourless, highly-refracting oil; b.p. 290° (corr.); and of sp.gr. 1·10228 at 15°. It has a bitter taste, savouring of peppermint, and a characteristic smoky smell. It is only slightly soluble in water, but freely soluble in alcohol or acetic acid. Its most characteristic reactions are the intense blue-green colouration which it gives with ferric chloride in alcoholic solution, and the insoluble compounds it forms with the alkalis and alkaline earths. Heated with hydrochloric acid at 140° it is decomposed with formation of methyl chloride, and a crystalline product (m.p. 80°) identical in composition and properties with the substance similarly obtained by Hofmann (Ber. 11, 329) from dimethylpropylpyrogallol. This resolution of picamar may be expressed by the equation

$$C_{10}H_{14}O_3+HCl=C_9H_{12}O_3+CH_3Cl.$$

The diaceto- derivative $C_{10}H_{12}(C_2H_3O)_2O_3$ is easily obtained by boiling picamar (one part) with acetic anhydride (two parts) for two hours. Recrystallised from alcohol, it is obtained in long colourless needles (m.p. 83°). This is converted by the action of bromine into the dibromo derivative $C_{10}H_{10}Br_2(C_2H_3O)_2O_3$. The potassium compound of picamar $C_{10}H_{12}K_2O_3$ is easily obtained by the addition of alcoholic potash to the alcoholic solution of the substance. The above results indicate that picamar is the monomethyl derivative of a higher homologue of pyrogallol, probably propylpyrogallol, and may be represented therefore by the constitutional formula: $MeO{\cdot}C_6H_2(C_3H_7)(OH)_2$.

PICEA. The spruce-firs: a genus of trees belonging to the conifers, the most important European member of which is the Norway Spruce (*P. excelsa*), constituting the 'White Norway,' Christiania, and Danzig deals of the timber merchant, much used for flooring, joists, and rafters. The waste portions of the trunks and smaller branches are made into splints for the match manufacturer (*v.* MATCHES). Spruce wood is also used in the manufacture of paper (*v.* CELLULOSE). 'Spruce rosin' or 'frankincense' is mainly obtained from *P. excelsa*, and is used in making the better varieties of Burgundy pitch (*v.* BURGUNDY PITCH). The bark and young cones of spruce are employed as tanning materials by the Norse peasantry and an infusion of the buds in milk is used by them as a remedy for scurvy. Spruce beer is made by adding a decoction of the green cone to the wort before fermentation. The needles of the Norway spruce, common silver fir (*Abies alba*), and some other conifers are used in the manufacture of 'pine wool' or 'forest wool,' which is spun and woven with cotton or wool to make 'hygienic flannel.' The black spruce (*P. nigra*) is chiefly found in Canada and Newfoundland. The spruce beer of America is made from the young shoots of this tree: the concentrated infusion of the buds constitutes 'Essence of Spruce.' Another species found in Canada is the White Spruce (*P. alba*).

Closely allied to *Picea* is *Tsuga*, including the Hemlock Spruce (*T. canadensis*), the bark of which is used for tanning.

Another ally is the Douglas fir (*Pseudotsuga Douglasii* and *P. macrocarpa*), which frequently rises to a height of 200 feet with a trunk measuring 8 to 10 in diameter: its timber is imported as Oregon pine.

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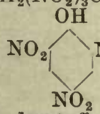
PICOLINE, PICOLINIC ACID *v.* BONE OIL.

PICOTITE *v.* CHROMITE.

PICRAMIC ACID *v.* NITROPHENOLS.

PICRIC ACID $C_6H_2(NO_2)_3OH$, or *symmetrical trinitrophenol*,  is the oldest artificial organic dyestuff, having been first prepared by Woulfe in 1771 by the action of strong nitric acid on indigo, who remarked upon its remarkable faculty for dyeing silk a bright yellow shade. Haussmann repeated this preparation in 1788, and investigated its acid properties, observing too its extremely bitter and nauseating taste (J. Phys. March, 1788). Welter obtained it later as a degradation product of silk with nitric acid (Ann. chim. Phys. [i.] 29, 301), and Liebig was the first to analyse the substance, describing its salts and giving it the name carbazotic acid (Schweigger's Ann. 47, 373). Its present name of *picric acid* (Greek πίκρος=bitter) is due to Dumas, who definitely established its composition. Laurent effected its synthesis from phenol and ascertained its chemical constitution (Ann. chim. Phys. [iii.] 3, 221).

Picric acid has been known in the literature under various names, such as yellow gall, bitter yellow, or as chrysolepinic acid, a name due to Schunck. Concerning picric acid there is an extensive bibliography, much of which is due to early workers at the beginning of last century, when the dyeing properties of this substance were considered important; only a selection of these references can be given here, along with the more recent investigations.

Preparation. For its laboratory preparation, one part of pure phenol is dissolved in an equal weight of concentrated sulphuric acid, and this solution added to 3 parts of nitric acid of sp.gr. 1·4 in small quantities at a time; after the first energetic action has subsided, the mixture is carefully heated on a water bath for 2 hours. On cooling, the product solidifies to a mass of crystals, which are collected, washed, and recrystallised from hot water (Laurent, Ann. Chim. Phys. [iii.] 3, 221).

It has been obtained by the action of hot nitric acid on *indigo* (Woulfe); *aloes* (Schunck, Annalen, 39, 7; 65, 234; *cf.* Marchand, J. pr. Chem. [i.] 44, 91); *Botany Bay* or *Acaroid resin*, the resin of *Xanthorrhœa hastilis* (R. Br.) (Stenhouse, Chem. Soc. Mem. 3, 10; Bolley, W. J., 1858, 460; Wittstein, Dingl. J. 216, 272); *gum benzoin* (Lea, Sillman's Amer. J. [ii.] 26, 381; Kopp, Ann. chim. Phys. [iii.] 13, 233); *salicin* (Piria, Annalen, 56, 63); *saligenin, salicylic acid, phlorizin, coumarin, balsam of Peru, tribromo-phenol*, the *nitrophenols*, and in general is the ultimate product of nitric acid upon most monophenolic substances (*cf.* Harding, Chem. Soc. Trans. 1911, 99, 1585).

Other interesting methods of formation are the following: oxidation of symmetrical trinitrobenzene with potassium ferricyanide; the acidic nature of the nitro groups facilitates the substitution of ·OH for H (Hepp, Ber. 1880, 13, 2346); aqueous sodium carbonate on picryl chloride (Ber. 1870, 3, 98; J. pr. Chem. [ii.] 1, 145).

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592); Powers and Rogerson (Pharm. J. 1909, iv. 29, 7; *ibid.* 1910, [iv.] 30, 326); Sani (Chem. Zentr. 1903, i. 93); Tarbouriech and Hardy (*ibid.* 1907, ii. 969); Sanders (Arch. Pharm. 1908, 246, 165); Matthes and Heintz (*ibid.* 1909, 247, 161); Klobb (Compt. rend. 1909, 149, 999); Power and Moore (Chem. Soc. Trans. 1909, 246, 1987); Dorée (*ibid.* 649); Rogerson (*ibid.* 1910, 1012); Menozzi and Moreschi (Chem. Zentr. 1910, i. 1777).

Extraction. The seeds, bark, or leaves are treated with ligroin, the solution is then evaporated, the residue dried between filter paper and crystallised from alcohol. From oils and fats phytosterol is obtained by saponification with alcoholic alkali and subsequent extraction with ether (Raumer, Zeitsch. angew. Chem. 1898, 24, 555; Wolf, Chem. Zeit. 1898, 22, 805; Heiduschka and Gloth, Pharm. Zentr.-h. 1909, 50 333). Phytosterol crystallises in needles and in plates, is soluble in chloroform, but insoluble in water and in alkalis and gives the same reaction as cholesterol with chloroform and sulphuric acid. It has m.p. 132°–136°, but this, as well as its constitution, varies with the source from which it is obtained.

Windaus and Hauth have resolved the crude phytosterol of calabar beans into two constituents: (1) *stigmasterol* or *β-phytosterol*, $C_{30}H_{50}O,H_2O$ or $C_{30}H_{48}O,H_2O$, m.p. 170°; $[\alpha]_D$–45·01° at 21° in $CHCl_3$, which gives a sparingly soluble *bromide* and an *acetate*, m.p. 141°, and a *tetra-bromo-acetate* decomposing at 211°–212°.

(2) *Sitosterol* or *α-phytosterol*, $C_{27}H_{46}O$ or $C_{27}H_{44}O$, m.p. 136°–137° $[\alpha]_D$-34·4° in chloroform, which is identical with the phytosterol contained in wheat germs (Burian, Monatsh. 1897, 18, 551). It yields a readily soluble bromide, and when reduced with sodium and alcohol forms *dihydrophytosterol*, $C_{27}H_{48}O$, m.p. 175°, the dichloride of which on reduction yields *dihydrophytostene*, $C_{27}H_{48}$, m.p. 80°–81°. It is probable that most of the phytosterols of m.p. about 135° consist entirely or chiefly of sitosterol (Ber. 1906, 39, 4378; *ibid.* 1907, 40, 3681; Pickard and Yates, Chem. Soc. Trans. 1908, 1929; Windaus and Welsch, Ber. 1909, 42, 612). According to Thoms (Arch. Pharm. 1897, 235, 39), the term phytosterol should be given to all unsaturated alcohols of high molecular weight, which give the characteristic cholesterol colour reactions and which owe their origin to physiological processes similar to those producing cholesterol.

Phytosterol esters may be obtained by heating the alcohol with 5 times its weight of the required acid or anhydride in a sealed tube on the water bath. The melting-points of some of the esters differ with the source of the phytosterol, but in all cases they are considerably higher than the corresponding cholesterol esters, and this can be used as one method of distinguishing between the two alcohols (Bömer and Winter, Zeitsch. Nahr. Genussm. 1901, 4, 865; Jaeger, Rec. trav. chim. 1907, 26, 311; Menozzi and Moreschi, *l.c.*); for other methods compare Kreis (Chem. Zeit. 1899, 23, 21); Ottolenghi (Atti. R. Accad. Lincei, 1906, [v.] 15, i. 44); Jaeger (Rec. trav. chim. 1906, 25, 334). The separation of phytosterol from cholesterol is based on the difference of the solubility of their dibromides in a mixture of ether and glacial acetic acid (Windaus, Chem. Zeit. 1906, 30, 1011). For the detection and estimation of phytosterol in fats, *see* Kreis and Wolf, Chem. Zeit. 1898, 22, 805; Foerster, *ibid.* 1899, 23, 188; Wirthle, *ibid.* 250; Kreis and Rudin, *ibid.* 986; Juckenack and Hilger, Arch. Pharm. 1898, 236, 367; Ritter, Chem. Zeit. 1901, 25, 872; *ibid.* 1902, 26, Rep. 100.

For other literature on phytosterol, compare Power and Tutin (Chem. Soc. Trans. 1908, 909); Molinari and Fenaroli (Ber. 1908, 41, 2785); Heiduschka and Gloth (Chem. Zentr. 1908, ii. 1519).

PICAMAR $C_{10}H_{14}O_3$ is easily obtained from wood tar; preferably from birch tar, which contains it in largest quantity. It is isolated by means of its potassium compound, which is purified by recrystallisation and decomposed by an acid; is a colourless, highly-refracting oil; b.p. 290° (corr.); and of sp.gr. 1·10228 at 15°. It has a bitter taste, savouring of peppermint, and a characteristic smoky smell. It is only slightly soluble in water, but freely soluble in alcohol or acetic acid. Its most characteristic reactions are the intense blue-green colouration which it gives with ferric chloride in alcoholic solution, and the insoluble compounds it forms with the alkalis and alkaline earths. Heated with hydrochloric acid at 140° it is decomposed with formation of methyl chloride, and a crystalline product (m.p. 80°) identical in composition and properties with the substance similarly obtained by Hofmann (Ber. 11, 329) from dimethylpropylpyrogallol. This resolution of picamar may be expressed by the equation

$$C_{10}H_{14}O_3+HCl=C_9H_{12}O_3+CH_3Cl.$$

The diaceto- derivative $C_{10}H_{12}(C_2H_3O)_2O_3$ is easily obtained by boiling picamar (one part) with acetic anhydride (two parts) for two hours. Recrystallised from alcohol, it is obtained in long colourless needles (m.p. 83°). This is converted by the action of bromine into the dibromo derivative $C_{10}H_{10}Br_2(C_2H_3O)_2O_3$. The potassium compound of picamar $C_{10}H_{12}K_2O_3$ is easily obtained by the addition of alcoholic potash to the alcoholic solution of the substance. The above results indicate that picamar is the monomethyl derivative of a higher homologue of pyrogallol, probably propylpyrogallol, and may be represented therefore by the constitutional formula: $MeO{\cdot}C_6H_2(C_3H_7)(OH)_2$.

PICEA. The spruce-firs: a genus of trees belonging to the conifers, the most important European member of which is the Norway Spruce (*P. excelsa*), constituting the 'White Norway,' Christiania, and Danzig deals of the timber merchant, much used for flooring, joists, and rafters. The waste portions of the trunks and smaller branches are made into splints for the match manufacturer (*v.* MATCHES). Spruce wood is also used in the manufacture of paper (*v.* CELLULOSE). 'Spruce rosin' or 'frankincense' is mainly obtained from *P. excelsa*, and is used in making the better varieties of Burgundy pitch (*v.* BURGUNDY PITCH). The bark and young cones of spruce are employed as tanning materials by the Norse peasantry and an infusion of the buds in milk is used by them as a remedy for scurvy. Spruce beer is made by adding a decoction of the green cone to the wort before fermentation. The needles of the Norway spruce, common silver fir (*Abies alba*), and some other conifers are used in the manufacture of 'pine wool' or 'forest wool,' which is spun and woven with cotton or wool to make 'hygienic flannel.' The black spruce (*P. nigra*) is chiefly found in Canada and Newfoundland. The spruce beer of America is made from the young shoots of this tree: the concentrated infusion of the buds constitutes 'Essence of Spruce.' Another species found in Canada is the White Spruce (*P. alba*).

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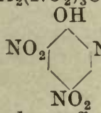

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An increased yield of picric acid is said to be obtained by heating phenol with pyrosulphuric acid at 100°-110°, and nitrating the resulting phenoltrisulphonic acid at 100° by the gradual addition of the calculated quantity of sodium nitrate (Eisenmann and Arche, D. R. P. 51321 of May 8, 1889; Eng. Pat. 4539 of 1889).

E. de Lom de Berg has patented a method for the preparation of picric acid from crude phenol (D. R. P. 51603 of June 9, 1889; Eng. Pat. 18904 of 1889). The crude material is either fractionally sulphonated—the first fractions consisting of phenolsulphonic acid, which is subsequently nitrated—or converted wholly into sulphonic acid, and the mixture of sulphonic acids fractionally nitrated, the last fractions consisting of picric acid. The sulpho derivatives of the cresols are very soluble in water.

Köhler (D. R. P. 67074; Frdl. 1890-1894, 804) describes a process consisting of heating 100 parts phenol with 1000 parts concentrated sulphuric acid for 2 hours at 170°, which gives rise to phenol disulphonic acid; 96 parts (1 molecule) of dry powdered Chile saltpetre are now added and heated to 140°. This nitrophenol-disulphonic acid is diluted with 320 parts of water and heated to 80°-90° with 244 parts Chile saltpetre, allowing the temperature to reach 140° in about 2 hours.

Gutensohn (D. R. P. 126197; Frdl. 1900-1902, 116) proposes to obviate the explosive violence of the direct nitration of phenol by adding a solution of phenol in heated paraffin oil, or other similar mineral oil, to strong nitric acid which has also been covered by a layer of paraffin, further quantities of this oil being added from time to time to dissolve all the phenol.

Wichardt (Fr. Pat. 345441 of 1904; Frdl. 1905-1907, 131) suggests a method of preparing picric acid without external heating, by admixture with aliphatic alcohols. A 95 p.c. yield is obtained when 20 parts phenol are mixed by constant stirring, with 100 parts nitric acid (sp.gr. 1·4) and 30 parts alcohol. Crude picric acid separates on cooling.

Wenghöffer (D. R. P. 125096; Eng. Pat. 16371 of 1900; Frdl. 1900-1902, 115) has used aniline as the initial material, converting this into sulphanilic acid, and treating the diazotised product with nitric acid; 50 grams aniline yield 110 grams picric acid.

In the process of Wolffenstein and Böters (D. R. P. 194883; Eng. Pat. 17521 of 1907; Frdl. 1908-1910, 141, 142) 400 grams benzene, 1350 grams nitric acid (sp.gr. 1·39), and 50 grams mercuric nitrate are mixed and warmed on the water-bath. The products are 380 grams picric acid, 160 grams nitrobenzene, 2 grams *o*-nitrophenol. The nitrobenzene is removed by distillation, leaving crude picric acid as the residue. Oxides of nitrogen may be substituted for nitric acid in presence of either mercury or its salts (D. R. P. 214045).

The Government regulations for the manufacture of picric acid regard it as an explosive except when it contains not less than half its weight of moisture.

Properties. Picric acid crystallises from water or alcohol in lustrous, bright-yellow leaflets, and from ether in rhombic prisms melting at 122·5°; it sublimes when cautiously heated, but explodes if heated rapidly (Berthelot, Ann. Chim. Phys. [vi.] 16, 21).

It is sparingly soluble in cold, but more readily soluble in hot, water, 1 part of the acid dissolving in 166 parts of water at 5°, in 86 parts at 15°, 81 parts at 20°, 77 parts at 22·5°, 73 parts at 26°, and in 26 parts at 79° (Marchand, J. pr. Chem. [i.] 44, 92).

The solution is more intensely coloured than the ordinary crystallised salt, and dyes the skin and animal fibres a deep yellow; 1 m.g. of acid in a litre of water colours the solution quite appreciably.

Picric acid dissolves readily at ordinary temperatures in alcohol or moist ether, and in about 10 parts of benzene; it is also soluble in concentrated sulphuric acid, forming a colourless solution, from which the picric acid may be partially precipitated on dilution.

Picric acid can be obtained in *colourless* crystals on recrystallising from concentrated hydrochloric acid (W. Marckwald, Ber. 1900, 33, 1128). By washing these crystals with water they develop a yellow colour, and the almost colourless mother liquor also becomes yellower on dilution with water. If ordinary picric acid be dried over concentrated sulphuric acid in a vacuum desiccator, it gradually assumes a lighter colour, and ultimately becomes almost colourless. Pure and perfectly dry picric acid may therefore be considered a colourless compound.

It has been proposed to explain these facts by the dissociation theory; as with other strong acids, ionisation is effected in presence of a mere trace of water, forming $C_6H_2(\overline{N}\dot{O}_2)_3O$— and $\overset{+}{H}$, the former complex ion being yellow. If, however, to this ionised solid or to its aqueous solution another strong acid like hydrochloric or sulphuric acid is added, then the picric ions associate again, the complex ions disappear as such, and the solution becomes paler. Ordinary or moist picric acid and the fused acid are both yellow; even specimens of the almost colourless acid give an intensely yellow melt. A striking illustration of these facts may be obtained by shaking commercial picric acid with light petroleum; as the solvent is a non-dissociating medium a colourless solution is obtained, containing, however, only little picric acid. If the colourless petroleum solution be now shaken with water, the solution becomes intensely yellow. Nearly colourless picric acid separates from hot concentrated solutions of light petroleum as white crystals on cooling. Similar bleaching effects on desiccation have been observed on fabrics themselves dyed with picric acid by Dreaper and Stokes (J. Soc. Dyers, Col. 1909, 25, 10).

Anhydrous ethyl ether dissolves picric acid only sparingly, and the solution is colourless until a trace of water be admitted, when the colour develops, and much more picric acid can now be dissolved in the moist ether (Bougault, J. Pharm. Chim. 1903, [iii.] 18, 116).

It has been stated by Vignon (Compt. rend. 1909, 148, 844) that the depth of colour of a picric acid solution varies according to its conductivity. Aqueous solutions dye wool and then become impoverished when their conductivity diminishes to a certain value. This impoverishment can also be brought about by adding hydrochloric acid. The fixation of the dye on the fibre Vignon ascribes to the action of the highly ionised dyestuff, the complex coloured ions combining with the fibre; it would seem, therefore, to be not a salt-forming phenomenon (*cf.* von Georgievics, Ber. 1906, 39, 1536; Sommerhoff, Zeit. Farb. Ind. 1906, 5, 270).

Stepanoff (Annalen, 1910, 373, 219) states that the solubility of picric acid in water decreases by the addition of hydrochloric acid, until it reaches a minimum when the solution contains roughly 0·5 millimolecule of picric acid and 150 millimolecules of the mineral acid in 100 c.c. of solution, after which the solubility increases as the concentration of hydrochloric acid becomes greater. He explains this change as being due to an additive compound of picric acid and hydrochloric acid, which is stable only in definite concentrations of hydrochloric acid, and dissolves readily in this acid when the concentration favourable to the existence of the addition compound is reached (*cf.* also J. Russ. Phys. Chem. Soc. 1910, 42, 495).

Other solubility measurements in various media, and various other physical properties, have been observed by Findlay (Chem. Soc. Trans. 1902, 81, 1219), Sisley (Bull. Soc. chim. 1902, [iii.] 27, 901), Marchand (J. pr. Chem. 1848, [i.] 44, 91), Dolinsky (Ber. 1905, 38, 1835), Drucker (Zeitsch. physikal. Chem. 1903, 46, 827; 1904, 49, 563), Bougault (J. pharm. Chim. 1903, [vi.] 18, 116), Gorke (Zeitsch. physikal. Chem. 1908, 61, 495).

Addition-compounds. Picric acid possesses the property of combining in molecular proportions with many aromatic hydrocarbons and phenols, giving crystalline additive compounds with a fair degree of stability (Fritzsche, J. pr. Chem. [i.] 73, 212; Annalen, 109, 247; Berthelot, Bull. Soc. chim. 1867, 7, 30).

Benzene forms such an addition product $C_6H_6, C_6H_2(NO_2)_3OH$, which crystallises in yellow needles, m.p. 85°–90°; it decomposes at the ordinary temperature in a vacuum desiccator, or by solution in water.

Naphthalene forms a molecular compound on fusion with picric acid or on mixing alcoholic solutions of the two components, yielding golden-yellow crystals, m.p. 149·5°; several eutectic mixtures may also be obtained. It is decomposed by large excess of alcohol (Saposchnikoff and Rdultowsky, J. Russ. Phys. Chem. Soc. 1903, 35, 1073).

The *anthracene* derivative is obtained by mixing concentrated alcoholic solutions of the hydrocarbon and acid, when beautiful ruby-red needles separate having the m.p. 138°; it is resolved into its components on dissolving in a large volume of alcohol, water, or ether (*cf.* Behrend, Zeitsch. physikal. Chem. 1894, 15, 183).

Phenanthrene yields a stable picric acid derivative, which may be recrystallised from alcohol and obtained in golden yellow crystals, m.p. 143° (Hayduck, Annalen, 1873, 167, 177). Ammonia liberates the hydrocarbon in the pure state, affording a means of separation of phenanthrene from anthracene.

Phenol and picric acid form an additive compound which melts at 53°; it decomposes at 100° or in a desiccator over sulphuric acid at ordinary temperatures (Goedike, Ber. 1893, 26, 3042). The same author has made a picrate of *acetophenone*, and suggests the rule that substituted phenols, &c., only form picrates when the substituent is in the *ortho*-position.

α-Naphthol picrate

$$C_{10}H_7(OH),C_6H_2(NO_2)_3OH$$

crystallises in orange-yellow needles, m.p. 189°, and is very soluble in alcohol or ether.

The *β-naphthol* derivative exists as yellow needles, m.p. 155°, readily soluble in alcohol, ether, or chloroform, although decomposed by ammonia. Combination is said to take place according to the law of adsorption, as the amount of compound formed depends on the concentration of the hydrogen ions (Pelet-Jolivet and Henny, Bull. Soc. Chim. 1909, [iv.] 5, 623; *cf.* also Kuriloff, Zeitsch. physikal. Chem. 1897, 23, 90, 673; 24, 441; and Bruni, Gazz. chim. ital. 1898, 28, ii. 508).

It has been shown by Bruni and Tornani (Chem. Zentr. 1904, ii. 954) that compounds possessing an allyl grouping, $\cdot CH_2\cdot CH:CH_2$ in the side chain, like safrol, methyl eugenol, and apiol, do not combine with picric acid, whilst compounds containing the propenyl grouping $-CH{=}CH\cdot CH_3$ react readily. Dioxymethylene compounds like piperonal, and ketones such as cyclohexanone also form well-defined picrates. Gibson describes the picrate of nitroaniline (Chem. Soc. Trans. 1908, 93, 2100), and Tilden and Forster have prepared a crystalline derivative of *pinene* and picric acid, m.p. 133° (Chem. Soc. Trans. 1893, 63, 1388).

In addition to the above additive products, picric acid forms very characteristic crystalline derivatives with most organic bases like pyridine and the alkaloids, and therefore provides a ready and valuable means for their purification and identification.

Reactions. Phosphorus pentachloride converts picric acid into trinitrochloro-benzene, or picryl chloride, m.p. 83°. Ferrous salts or alcoholic ammonium sulphide reduce the acid to dinitro-aminophenol, or picramic acid, m.p. 168°–169°, which was formerly used as a brown dye (Girard, Compt. rend. 36, 421); whilst aqueous ammonium sulphide reduces it to diaminonitrophenol (Griess, Annalen, 1869, 154, 202). Complete reduction of all the nitro groups is effected by tin and hydrochloric acid, the triaminophenol thus formed being characterised by the deep blue colour which it gives in aqueous solution with ferric chloride (Roussin, Wagner's J., 1861, 536).

A hot solution of picric acid reacts with potassium cyanide forming a strongly coloured, brown-red solution of picrocyaminic or *iso*purpuric acid, $C_6H_2(NO_2)_2N(CN)_2OH$, formerly known as a dyestuff, grenat brown (Hlasiwetz, Annalen, 1859, 110, 290; Zulkowsky, Wagner's J., 1868, 661; Kopp, Ber. 1872, 5, 664). A like reaction occurs with the cyanides of all the alkalis and alkaline earth metals, and with magnesium, cadmium, and zinc, whilst silver, copper, and mercury cyanides do not show this reaction (Varet, Compt. rend. 112, 339; 119, 562).

Borsche has contributed to our knowledge of this as a general reaction for nitrophenols (Ber. 1900, 33, 2719, 2995; 1903, 36, 4357; 1904, 37, 1843, 4388), and ascribes to *iso*purpuric acid the constitution

$$C_6(NO_2)_2(CN)_2(OH)NH{\cdot}OH.$$

Boiling picric acid with alkalis seems to eliminate one nitro group as ammonia, and both prussic acid and a nitrite can be detected in the aqueous solution as alkali salts (Wedekind and Haeussermann, Ber. 1902, 35, 1133). Oxidation with hydrogen peroxide in presence of ferrous salts yields an intense green solution, and the product reacts with phenylhydrazine (Fenton and Jones, Chem. Soc. Trans. 1900, 77, 76). Oxidation with chromic acid causes no liberation of nitrogen (Oechsner de Coninck and Combe, Compt. rend. 1899, 128, 239).

Sodium carbonate seems to possess a specific property of precipitating sodium picrate from solution. A single drop of a cold saturated solution of a picrate added to 10 c.c. of a 1 p.c. solution of the carbonate produces a slight turbidity, and with increasing concentration of the carbonate solution, or larger quantities of the picrate, the phenomenon becomes still more conspicuous (Reichard, Zeitsch. anal. Chem. 1904, 43, 269). The potassium salt is very sparingly soluble, and for this reason serves as a qualitative test for potassium.

A *hydrazine picrate* $C_6H_2(NO_2)_3OH,N_2H_4$ is described by Silberrad and Phillips (Chem. Soc. Trans. 1908, 93, 474). Picric acid stains may be removed by a solution of alkaline sulphide or polysulphide, followed by a thorough washing with soap and water (Bougault, J. Pharm. Chim. 1903, 18, 158).

Detection and estimation. Picric acid is not volatile in steam, and can readily be detected by its bitter taste and the sparing solubility of its potassium salt. The usual tests are five in number, and are given below, with their limits of sensitiveness subjoined: I. The *iso*purpuric acid reaction, showing a blood-red colouration on warming picric acid with potassium cyanide and soda; limit, 1 : 5000. II. The picramic acid reaction, giving rise to a blood-red colour on heating with sodium hydroxide and grape sugar; limit, 1 : 7000. III. Picramic acid reaction with sodium hydroxide and ammonium sulphide; limit, 1 : 12,500. IV. Yellowish-green crystalline precipitate of hexagonal needles, which polarise light, is obtained when ammoniacal solution of copper sulphate is added to picric acid in water; limit, 1 : 80,000. V. By dyeing white wool; degree of delicacy is 1 : 110,000. The reactions II. and V. are less sensitive in presence of fats or other impurities. Rymsza (Zeitsch. anal. Chem. 1897, 36, 813) describes a method of extracting and treating mixtures containing picric acid only in traces in order that the above tests may subsequently be applicable. The method consists in macerating the substance with dilute sulphuric acid, mixing with 3 volumes of 95 p.c. alcohol and digesting for 24 hours at 50°–60°. After filtration and evaporation of the alcohol, any fat is removed by shaking with light petroleum, and the liquid is then acidified with hydrochloric acid and extracted repeatedly with ether. In cases of picric acid poisoning the urine is always coloured red-brown by presence of picramic acid; the picric acid may be extracted with ether after simply acidifying, and the above tests, preferably I., applied.

An aqueous solution of picric acid gives with methylene blue, in the cold, a violet flocculent precipitate, soluble in ether, chloroform, or hot water. These coloured solutions vary from blue to green. When the solution in chloroform is evaporated, a violet residue is obtained (Swoboda, Chem. Zentr. 1896, ii. 717; Zeitsch. anal. Chem. 1897, 36, 513). Lacquers tested in this way for picric acid should first be dissolved in a little alcohol. It is claimed that the picramic acid test (II. and III.) is sensitive to 1 part per hundred thousand if the reduction is effected with sodium hyposulphite in presence of ammonia (Aloy and Frébault, Bull. Soc. chim. 1905, [iii.] 33, 495).

Picric acid differs from the nitrocresols in the colourations of its reduction products with stannous chloride and hydrochloric acid.

Rupeau describes the application of the *iso*purpuric acid test (I.) for the colorimetric estimation of picric acid in beer; it is claimed that 0·01 gram of acid per litre may thus be recognised (Chem. Zentr. 1897, ii. 813). A reagent is suggested consisting of 5 grams ferrous sulphate, 5 grams tartaric acid, and 200 c.c. of a brine solution; 0·5 gram of the sample of beer is allowed to flow on to 1–2 c.c. of the above reagent, and 2 drops of ammonia are added, and the mixture gently shaken. A reddish colouration appears, sensitive to 0·005 gram picric acid per litre.

Schwarz (Monatsh. 1898, 14, 139) has used a volumetric method for the determination of nitro derivatives generally, depending upon the liberation of iodine by heating in a closed vessel at 100° with an iodate and iodide. This has been improved by Feder (Chem. Soc. Abstr.

1906, ii. 809), who merely mixes potassium iodide and iodate with the picric acid solution, iodine being liberated, which is estimated by titrating with thiosulphate, using starch solution as indicator. For the evaluation of picric acid salts it is necessary to acidify with mineral acid, extract with benzene, evaporate, and redissolve the residue in water before proceeding with the above titration. The use of a potassium iodide solution after bromination with bromine water, in order to determine the amount of halogen absorbed, is recommended by Allen (Chem. Soc. Trans. 1888, 53, 592). Sinnatt has employed Knecht's method of titration with titanous chloride for the estimation of the additive compound with naphthalene (Chem. Soc. Proc. 1905, 18, 297; *cf.* Colman and Smith, Chem. Soc. Trans. 1900, 77, 128). Picric acid in its compounds with organic bases has been estimated colorimetrically by Kutusow (Zeitsch. physiol. Chem. 1894, 20, 166); *e.g.* ptomaines are readily separated from mixtures by the addition of picric acid and the compound can be weighed; but the author recommends the determination of the combined picric acid colorimetrically either by the spectrophotometer, or, better, by the use of Hoppe-Seyler's double pipette (*cf.* Zeitsch. physiol. Chem. 16, 505).

A gravimetric determination of picric acid is given by Busch and Blume (Zeitsch. angew. Chem. 1908, 21, 354), depending upon the precipitation of nitron-picrate, and involving the use of the reagent 'nitron' (described in Ber. 1905, 38, 856). Nitron picrate, which is very sparingly soluble, consists of lemon-yellow needles, and after drying at 110° is weighed; the weight multiplied by $\frac{229}{541}$ gives the amount of picric acid present in the solution examined. The method is not applicable in presence of hydrobromic, hydriodic, chloric, perchloric, nitrous, nitric, or chromic acids.

An alternative method of evolution, due to Utz (Zeitsch. anal. Chem. 1908, 47, 140), is recorded, in which picric acid is oxidised with hydrogen peroxide in sodium hydroxide solution, and the nitric acid produced is precipitated as insoluble nitron-nitrate and subsequently weighed: 1 gram$=$0·037406 gram of nitrogen.

Picric acid may be quantitatively estimated by precipitation with acridine, since acridine picrate is very sparingly soluble in cold water (Anschütz, Ber. 17, 439).

Adulterations. Commercial picric acid sometimes contains impurities, which either are by-products—*e.g.* resin, oxalic acid, &c.—formed in its manufacture and insufficiently removed by washing, or are fraudulent additions. According to Winckler (Wagner's J., 1858, 461), the following impurities may be recognised thus:—(1) Resin: dissolve 1 part of picric acid in 60 parts of boiling water, add $\frac{1}{20000}$ of the weight of sulphuric acid and filter. Any resin will be left behind on the filter paper. (2) Oxalic acid: examine the specimen microscopically, or dissolve 1 part in 100 parts of water, and estimate the amount by precipitating with ammonia and calcium chloride solution. (3) Nitre, or sodium sulphate: treat with alcohol to dissolve the picric acid present, and examine the saline residue by the ordinary method. (4) Sugar: neutralise with potassium carbonate, evaporate to dryness, and extract the sugar by repeated treatment with alcohol; then examine the alcoholic extract for sugar in the usual way.

Casthélaz (Chem. News, 15, 140) states that common salt and alum are sometimes used as adulterants in addition to the foregoing, and treats the specimen with benzene or ether, which extract the whole of the picric acid, but do not dissolve the oxalic acid and various salts which may be present.

Uses in Industry

Dyeing. Picric acid has the property of dyeing animal fibres and tissues directly in an acid bath, but is not fixed by cotton or other vegetable fibres, unless previously mordanted with albumen or with a mixture of aluminium and magnesium acetates; hence it is sometimes used as a means of detecting cotton in undyed silk or woollen fabrics. Its tinctorial powers are great, and it produces on silk and wool a clear, bright yellow, which, compared with most other yellows, appears to have a greenish shade; but, owing to the colour being fast neither to light nor washing, picric acid is now but little used as a yellow dye, although it is frequently employed to produce compound colours with such dyes as benzaldehyde-green, methyl-violet, indigo-carmine, &c.

Picric acid has been used in the preparation of certain other dyestuffs of the nigrosine and induline class; it is fused with various monamines such as aniline and its hydrochloride, in presence of ammonium vanadate, and the spirit-soluble dye converted into water-soluble dye by sulphonation and formation of the sodium salt; a nigrosine colouring matter results. The indulines involve the use of aromatic diamines in a similar manner, and glycerol is added to the melt (D. R. PP. 84293, 84294; Frdl. 1894–1897 449, 451; *cf.* also Bacovescu, Chem. Zentr. 1908, i. 2034).

Substantive cotton dyes have been prepared from picric and picraminic acids by heating in aqueous solution with sulphur and alkaline sulphides (D. R. P. 116791; Frdl. 1900–1902, 740).

Tanning. Its use in the leather industry is mentioned by Watenburger (Leather Manufacture, 1901, 12, 54; J. Soc. Chem. Ind. 1901, 596). After tanning the hides with picric acid solution, they are allowed to drain and then transferred to a 1 p.c. tannin extract for 12 hours; they are afterwards washed, partially dried and fat liquored, and finished in the usual way. The picric acid is fixed in the grain of the material in a permanently insoluble form.

Explosives. Picric acid is usually said to explode on heating, but Berthelot has pointed out (Compt. rend. 105, 1159) that this is only true when very small quantities at a time are suddenly heated, for when heated in any quantity the acid melts and gives off vapours which burn with a luminous flame without explosion; picric acid, moreover, does not under ordinary conditions explode by percussion. The picrates, on the other hand, are readily exploded by heating or percussion, and have been employed as explosives—lead picrate, for example, being used for filling percussion caps (Prat, J. 1874, 1124). Picrates, however, do not contain sufficient oxygen for their complete combustion, and hence mixtures of potassium or ammonium picrate with either nitre or potassium chlorate have been employed (Wagner's J. 1871, 318)—Brugères' picrate powder, for example, consisting of 54 p.c. ammonium picrate and 46 p.c. potassium nitrate (Compt. rend. 69, 716). The volumes of gas liberated by the explosion of lead, strontium, barium, and potassium picrates respectively, and of mixtures of potassium picrate with 45 p.c. of nitre or 50 p.c. of potassium chlorate, have been measured by Roux and Sarrau (Compt. rend. 77, 478; 79, 757), and the volume and composition of the gas, together with the composition of the residue produced by the explosion of potassium picrate under varying pressures, have been determined by Sarrau and Vieille (Compt. rend. 93, 61).

Mixtures of picric and various oxidising agents have been proposed as explosives. Thus a solution of 58·3 parts of picric acid and 41·7 parts of nitric acid (sp.gr. 1·5) explodes with great violence and without smoke when fired with a detonator (Sprengel, Chem. Soc. Trans. 1873, 800), and mixtures of analogous composition stiffened with asbestos have been patented by Punshon (Eng. Pat. 2242 of 1880, 11432 of 1885) whilst Tschirner has patented an explosive consisting of 1 part picric acid, 1 part coal-tar, and 5 parts potassium chlorate (or potassium permanganate in about the same proportion), which is fired by percussion caps (D. R. P. 15508 of Feb. 6, 1880). These mixtures with oxidising agents have the double effect of decreasing the force of the explosion, and at the same time increasing the sensitiveness of picric acid to detonation. Mélinite, one of the most powerful explosives invented, is said to consist solely of compressed picric acid. According to Turpin (Eng. Pat. 15089 of 1885; D. R. P. 38734 of Jan. 12, 1886; Zeitsch. Chem. Ind. 1, 193), picric acid, when obtained in masses (1) by compression, (2) by admixture with gum arabic solution or with a suitable fat or oil, or (3) by admixture with 3–5 p.c. of collodion, can be exploded in closed vessels by 1–3 grams of silver fulminate. The best results and the greatest insensitiveness are attained by fusion of the acid, since a mass of fused picric acid cannot be exploded in the open air by detonation with 3 grams of silver fulminate introduced into the interior, although shells, torpedoes, &c., filled with liquid picric acid (fused at 130°–145°), and cooled slowly, can be exploded by a charge of quick-burning gunpowder or a priming of picric acid powder detonated by 1·5 grams of fulminate, the explosion being one of the most destructive known.

An account of the most important metallic salts with their characteristic properties is given below. Their chief interest lies in the explosive nature of these derivatives of picric acid (*v.* EXPLOSIVES).

SALTS OF PICRIC ACID.

The metallic salts may be prepared by bringing together picric acid and the carbonate or oxide of the metal, and evaporating the solution until crystals appear on cooling. The references to the literature on this section of the subject are too numerous to be given, and, moreover, the results published by different workers are not always concordant. An excellent *resumé* and bibliography is given in a paper by Silberrad and Phillips (Chem. Soc. Trans. 1908, 93, 474), who reinvestigated several of the metallic salts.

Aluminium salt $[C_6H_2(NO_2)_3O]_3Al,16H_2O$. Pale yellow needles. Changes to *tetrahydrate* at 80°, which is a pale yellow powder decomposing without explosion on heating.

Ammonium salt exists as a yellow and red variety, both anhydrous. They volatilise without detonation on heating. Soluble in water, sparingly so in alcohol.

Barium salt $[C_6H_2(NO_2)_3O]_2Ba,5H_2O$. Deep yellow prisms, sparingly soluble in cold water. It becomes *anhydrous* on heating at 80°, giving a yellow powder which explodes with violence at 333°.

Cadmium salt $[C_6H_2(NO_2)_3O]_2Cd,7H_2O$. Yellow hexagonal plates; yields the *anhydrous* salt at 80°, which is yellow and explodes violently at 336°. A pentahydrate also exists.

Calcium salt $[C_6H_2(NO_2)_3O]_2Ca,10H_2O$. Yellow plates; yields *anhydrous* salt at 80°, which is a yellow powder exploding with violence at 323°. A *pentahydrate* is known.

Chromium salt is basic and of complex constitution. Green crystals.

Cobalt salt $[C_6H_2(NO_2)_3O]_2Co,9\frac{1}{2}H_2O$. Brown needles. The *hexahydrate* is better known and exists as brown laminæ. Both these give the dihydrate at 80°, and the *anhydrous* salt at 150°, the latter being a brown powder exploding at 320°.

Copper salt $[C_6H_2(NO_2)_3O]_2Cu,11H_2O$. Green prisms, which yield the *anhydrous* salt at 80°. This latter is a greenish-yellow powder, exploding violently at 282°.

Ferric salt $[C_6H_2(NO_2)_3O]_3Fe,11H_2O$. Reddish-yellow crystals.

Ferrous salt $[C_6H_2(NO_2)_3O]_2Fe,8H_2O$. Obtained from barium salt and ferrous sulphate. Yellow hexagonal prisms. Becomes *anhydrous* in vacuum over sulphuric acid, yielding a dark green powder, which explodes feebly at 315°.

Lithium salt $C_6H_2(NO_2)_3OLi,4H_2O$. Yellow prismatic needles, changing gradually into the dark orange-yellow *monohydrate*. This becomes *anhydrous* at 150°, giving a pale yellow powder, which explodes at 318°.

Lead salt $[C_6H_2(NO_2)_3O]Pb,4H_2O$. Silky yellow needles, yielding monohydrate at 80°, and the anhydrous salt at 150°; the last of these is a yellow powder, which explodes violently at 270° and differs from all the other salts in being extremely sensitive to shock or friction.

Magnesium salt $[C_6H_2(NO_2)_3O]Mg,9H_2O$. Silky, yellow needles. Forms also a *hexahydrate* and *dihydrate*, all of which become anhydrous at 150°. Explodes feebly at 367°.

Manganese salt $[C_6H_2(NO_2)_3O]Mn,8H_2O$. Yellow prisms. At 80° forms *trihydrate*, and at 150° becomes anhydrous; this last is yellow, and explodes with violence at 325°.

Mercury salt $[C_6H_2(NO_2)_3O]_2Hg,4H_2O$. Difficult to prepare, as it tends to pass into the *basic hexahydrate*, the *anhydrous* salt of which volatilises without explosion on heating.

Nickel salt $(C_6H_2(NO_2)_3O]_2Ni,9\frac{1}{2}H_2O$. Green needles. *Hexahydrate* forms green laminæ

Both yield the dihydrate at 80°, and the anhydrous salt at 150°, the latter being a green powder, which explodes at 335°.

Potassium salt $C_6H_2(NO_2)_3OK$, is anhydrous. It crystallises from aqueous solutions in yellow iridescent prismatic needles, and explodes at 311°. Sparingly soluble in cold water.

Silver salt $C_6H_2(NO_2)_3OAg$. Yellow anhydrous salt, exploding feebly at 336°.

Sodium salt $C_6H_2(NO_2)_3ONa,H_2O$. Minute, yellow needles, yielding *anhydrous* salt at 150°, which is a pale yellow powder, exploding feebly at 310°.

Strontium salt $[C_6H_2(NO_2)_3O]_2Sr,5H_2O$, yellow needles, yields *monohydrate* at 80°, and *anhydrous* salt at 200°. Explodes violently at 340°.

Zinc salt $[C_6H_2(NO_2)_3O]_2Zn,9H_2O$. Yellow prismatic needles; yields *dihydrate* at 80°, and *anhydrous* salt at 150°, which is a brownish-yellow powder, exploding violently at 350°. The *hexahydrate* has been prepared and also an *octohydrate.*

Cf. paper by Kast (Chem. Soc. Abstr. 1911, 100, 852; Zeitsch. ges. Schiess-sprengstoffwesen, 1911. 6, 7).

A *sodium peroxide derivative* of picric acid $C_6H_2(NO_2)_3O—ONa$ has been patented as a very powerful explosive (D. R. P. 96855; Frdl. 1897–1900, 47). It is prepared by heating 5 grams of sodium peroxide in 200 c.c. of water containing 15·9 grams of picryl chloride for 2–3 hours. The solution becomes deep brown, and deposits red-brown prisms on cooling, which are sparingly soluble.

A picra-borate explosive, described by Billet (J. Soc. Chem. Ind. 1900, 1144), is obtained by heating aqueous solutions of sodium borate and picric acid.

Girard (J. Soc. Chem. Ind. 1900, 1144) gives a new method of preparing picrates for explosives: a mixture of 30 kilos. castor oil and 10 kilos. of powdered picric acid is incorporated with the theoretical quantity of the base in the state of carbonate or oxide; the soluble alkalis are used in solutions of 45°Bé. The oil should be present in not less amount than 5 parts to 10 parts of acid. Metallic oxides may be replaced by oleates, stearates, palmitates, &c., the fatty acids dissolving in the castor oil after reaction. The salts are dissolved out with volatile solvents to avoid the inconvenience attending their recovery from aqueous solution.

ETHERS OF PICRIC ACID.

Methyl picrate $C_6H_2(NO_2)_3OCH_3$ (*trinitroanisole*). Yellow monoclinic tables, m.p. 64° (Post and Mehrtens, Ber. 8, 1552; Frdl. 1879, 514). Obtained by nitrating anisole. Decomposed by strong potassium hydroxide giving picric acid, and with ammonia giving trinitraniline (Salkowski, Annalen, 1874, 174, 259).

Ethyl picrate $C_6H_2(NO_2)_3OC_2H_5$. Long, almost colourless needles, m.p. 78·5° (Stenhouse and Müllert, Annalen, 1867, 141, 80; Willgerodt, Ber. 1879, 12, 1277). Obtained from methyl ether on recrystallising from ethyl alcohol (Boos, Amer. Chem. J. 20, 449).

Phenyl picrate $C_6H_2(NO_2)_3OC_6H_5$. Needles, m.p. 153°. Prepared from picryl chloride and potassium phenate in aqueous alcoholic solution (Willgerodt, Ber. 1879, 12, 1278).

Acetyl picrate $C_6H_2(NO_2)_3O·OC·CH_3$. Deep yellow crystals, m.p. 75°. Decomposes, giving acetic acid, at 120°. Obtained from picric acid and acetic anhydride (Tommasi and David, Annalen, 169, 167; Heinke, Ber. 1898, 31, 1400; v. Pechmann, Ber. 1900. 33, 629). Very soluble in warm alcohol or ether.

OTHER DERIVATIVES.

Picyrl chloride $C_6H_2(NO_2)_3Cl$. Crystallises from ether in amber-yellow tables; from alcohol in almost colourless needles, m.p. 83°. Obtained by the action of phosphorus pentachloride on picric acid. Like picric acid itself, it combines with aromatic hydrocarbons, forming additive products (Pisani, Annalen, 1854, 92, 326; Liebermann and Palm, Ber. 1875, 8, 378).

Picryl bromide $C_6H_2(NO_2)_3Br$. Elongated, pale-yellow plates, m.p. 122°–123° (Jackson and Earle, Amer. Chem. J. 1903, 29 212). Obtained by nitrating bromobenzene.

Picramide $C_6H_2(NO_2)_3NH_2$ (trinitraniline). Prepared by action of ammonia on picryl chloride or on ethyl picrate. Dark yellow, monoclinic tables, m.p. 188° (Hepp, Annalen, 1882, 215, 350; Salkowsky, Annalen, 1873, 165, 187).

Picramic acid $C_6H_2(NO_2)_2(NH_2)OH$. Obtained by reduction of picric acid with ammonium sulphide or other mild reagents. Red crystals, m.p. 169° (Girard, Annalen, 1853, 88, 281; Pugh, *ibid.* 1855, 96, 83; Stuckenberg and Rudolf, J. pr. Chem. [ii.] 48, 425). Used formerly as a brown dye.

***iso*Purpuric acid** (picrocyaminic acid, or *grenat brown*) *v. iso*-PURPURIC ACID.

PICRIN *v.* DIGITALIS.

PICROGLYCION *v.* DULCAMARA.

PICROPODOPHYLLIC ACID and **PICROPODOPHYLLIN** *v. Podophyllum resin*, art. RESINS.

PICROTIN, PICROTOXIDE *v.* PICROTOXIN.

PICROTOXIN. A poisonous crystalline compound, somewhat allied in its physiological action to strychnine, which occurs in 'Cocculus Indicus,' the small, berry-like fruit of *Anamirta paniculata* (Colebrooke) (Bentl. a. Trim. 14), a climbing shrub of Eastern India and the Malayan islands. The drug does not find much favour in Western medicine, but is employed in India. Here it is better known for its power of stupefying fish and causing them to rise to the surface of the water in a state of intoxication, and as a reputed adulterant of malt liquors. On account of its poisonous properties, it sometimes becomes necessary to search for it in beer.

The small, black, ovoid fruit consists of a rough, tasteless pericarp, enclosing a reniform seed, which has an oily and bitter taste. The pericarp does not contain picrotoxin, but Pelletier and Couerbe isolated from it two crystalline compounds: *menispermine*, a base, which melts at 120° and forms a crystalline sulphate, and *paramenispermine*, a neutral constituent which melts at 250°, together with a brown mass, *hypopicrotoxic acid*, which softens at 100° (Ann. Chim. Phys. [ii.] 54, 196). Half the weight of the seed is stearin. The *picrotoxin* exists to the extent of 0·4 to 1·0 p.c. It was discovered in 1812 by Boullay (J. Pharm. Chim. [i.] 4, 5).

is effected by sublimation, treatment with alkalis, alkaline polysulphides, or the like.

Numerous other methods of manufacture have been suggested and practised. Vermilion possesses great opacity, but dries imperfectly in oil and is liable to separate from the vehicle used. It is permanent in oil, durable in tempera and fresco, but changeable in water colour by the influence of the solar rays. Sulphuretted hydrogen does not affect it, and in oil it can be mixed with all except certain copper pigments. As it is a volatile compound, it is ineligible for enamels and ceramic ware.

Brilliant scarlet, Royal scarlet, Pure scarlet, mercuric iodide, HgI_2: extremely brilliant as a pigment and of good body, but fugitive in oil, useless in water colour, immiscible with many other pigments, and too costly for practical purposes.

Mercurous chromate Hg_2CrO_4, and *mercuric chromate* $HgCrO_4$, red, highly alterable products, obtained in the wet way by double decomposition. Nearly valueless as pigments, although fine and attractive colours.

Pigments containing lead. Of high importance among the lead pigments and, indeed, among commercial pigments generally, is *white lead,* called also *Krems* or *Kremnitz white, Berlin white, Silver white, Cerussa alba, Céruse, Bleiweiss, Blanc de Plomb, Blanc d'argent,* and *Flake white,* $2PbCO_3,Pb(OH)_2$. This basic carbonate of lead is one of the most rapidly drying pigments commonly used in oil; it possesses great opacity and covering power, and is facile in working. Miscible with most durable colours, it promotes the drying of many which have slight siccative qualities of their own. Unfortunately, white lead is highly poisonous, its manufacture is attended with risk to the operatives, it is readily discoloured by sulphuretted hydrogen, and used with oil it emits a nauseous odour. Numberless substitutes have been proposed, of which perhaps lithopone, zinc oxide, and 'non-poisonous white lead,' are the best known. The supersession of lead products by zinc whites is undoubtedly extending apace.

'*Non-poisonous white lead,*' or *patent white lead,* and '*sublimed white lead*' are composed chiefly of lead sulphate, with small proportions of lead and zinc oxides. The last-named is a basic sulphate with some zinc oxide. These products are little affected by sulphuretted hydrogen, and are virtually non-poisonous: but the covering power of a lead sulphate pigment is less than that of white lead, and the drying quality is inferior.

Lead oxychloride $PbCl_2,PbH_2O_2$, sometimes called *Pattinson's white lead,* is occasionally used as a white pigment, as also have been the normal carbonate, sulphite, hydroxide, and other salts of lead. All are less satisfactory than the basic carbonate.

Turner's yellow, Cassel yellow, Montpellier yellow, or *Verona yellow,* $PbCl_2,7PbO$, is another basic lead chloride, now superseded by chrome yellows.

Massicot and *litharge* are, respectively, yellow and red modifications of lead monoxide, PbO. The monoxide is now scarcely used as a pigment, but as a drier is of considerable importance. Large quantities are used by potters, glassmakers, and rubber manufacturers.

Red lead, Orange lead, minium, mennige, Paris red, Pb_3O_4, sometimes Pb_4O_5, a fine orange-red pigment, which very quickly dries in oil but is discoloured by sulphuretted hydrogen, and is incompatible in admixture with certain sulphur-containing pigments, such as lithopone and cadmium yellow. As a priming coat, in conjunction with white lead for ordinary work, it is extremely useful. *Orange mineral* is a less dense form of red lead.

Sublimed blue lead is a mixture of basic sulphate, $2PbSO_4{\cdot}PbO$, with lead sulphide, sulphite, oxide, and carbon. It is used to a considerable extent as a protective pigment.

Pigments containing silver. The metal in a finely divided state has occasionally found employment as a pigment, and the use of the chromate, Ag_2CrO_4, has been proposed. Costliness and extreme sensitiveness to sulphuretted hydrogen, are sufficient deterrents to a common application of silver pigments.

Pigments containing copper. *Vandyke red,* copper ferrocyanide, Cu_2FeCy_6, is a brownish-red pigment, occasionally used in artistic painting, but it is untrustworthy and liable to darken.

Vert de Gris, Verdigris, Vert de Montpellier, Grünspan, basic copper acetate, varies in hue according to the basicity of the compound. Green verdigris, of the brightest tint, is $2Cu(C_2H_3O_2)_2{\cdot}CuO,6H_2O$; blue verdigris is $Cu(C_2H_3O_2)_2{\cdot}CuO,6H_2O$: but other basic acetates are known and the commercial pigment is a variable mixture of several of these salts. It is made by the action of acetic acid upon copper in the presence of air and moisture. This pigment is useless in water-colour painting, injured by sulphuretted hydrogen, carbon dioxide, and moisture, immiscible with sulphide and some other pigments, and is a powerful poison. In oil it dries well, but is only permanent if 'locked up' by the presence of a large quantity of a resinous varnish.

Mountain green, Green verditer, Malachite, Mineral green, or *Berggrün,* the natural green hydroxycarbonate of copper, $CuCO_3{\cdot}Cu(OH_2)$. This is the mineral malachite, finely ground, and is known to have been used by the Græco-Roman artists. As an oil-paint it is moderately durable, but it is liable to darken and assume a brownish or olive tint, and for water-colour it is unsuitable. It will blacken if mixed with cadmium yellow, ultramarine, &c., and is highly sensitive to sulphuretted hydrogen.

Schweinfurt green, Mitis green, Vert Paul Véronèse, Vert de Paris, Emerald green, cupric aceto-arsenite, $Cu(C_2H_3O_2)_2 3(CuAs_2O_4)$, is an exceedingly fine but very poisonous colour, prepared by heating together verdigris, water, and arsenious oxide, the precipitate formed being washed and dried. Inadvisable for use as a water-colour, it is durable in oils, but must not be mixed with sulphide pigments, such as cadmium yellow and ultramarine, nor exposed to sulphuretted hydrogen, which quickly darkens it. Emerald green is somewhat deficient in body and dries slowly. It is not trustworthy for tempera or fresco work.

Scheele's green, a basic copper arsenite, varying somewhat in composition, is a pale green pigment of an extremely poisonous character, and is now seldom used. Sulphuretted hydrogen and sulphide pigments are even more injurious to it than to Schweinfurt green.

Brunswick green was formerly basic chloride of copper, $CuCl_2 \cdot 3CuO,4H_2O$, now not used as a pigment. The name is now applied to a mixture of Prussian blue, chrome yellow and barytes.

Mountain blue, Blue verditer, Chessylite, Azurite, Blue ashes, or *Bergblau,* the natural blue hydroxycarbonate of copper, $2CuCO_3 \cdot Cu(OH)_2$. Both this and the green hydroxycarbonate (above described) have been artificially manufactured, but not with conspicuous success. Blue verditer is not permanent, and is a pigment little used, artificial ultramarine and cobalt having superseded it.

Lime blue and *Bremen blue* are essentially copper hydroxide, $Cu(OH)_2$, associated with calcium sulphate and copper carbonate respectively: both were formerly much used in decorative work. Blue lakes from coal-tar dyes and artificial ultramarine have virtually driven these pigments off the market.

Stannate, phosphate, borate, silicate, and other salts of copper have been tried as pigments, but not very successfully.

Pigments containing cadmium. *Cadmium yellow, pale cadmium, orange cadmium, Orient yellow, radiant yellow, aurora yellow,* &c., are cadmium sulphide, CdS. The cadmium pigments, if free from uncombined sulphur, may safely be mixed with white lead in oil; and, being themselves unaffected by sulphuretted hydrogen, they hinder the darkening of flake white by that gas. Light, air, and moisture have little effect upon the pure cadmium colours when used in oil-painting, but the paler shades are extremely fugitive in water-colour, and the presence of free sulphur is very detrimental since it enhances the tendency to fade. Cadmium pigments are entirely incompatible with the copper greens and blues, and exert a darkening action upon Naples yellow, chrome yellow, Cassel or Turner's yellow, and the like.

Neutral orange, Penley's neutral orange, is a mixture of cadmium sulphide with Venetian red.

Pigments containing bismuth. *Pearl white,* basic bismuth nitrate, $Bi(OH)_2NO_3$, or $[Bi(NO_3)_3 \cdot 2Bi(OH)_3]$, is of little value as a pigment, owing to its susceptibility to the action of sulphuretted hydrogen, which darkens it more rapidly than lead-compounds. Bismuth white was formerly used as a face-powder with somewhat doubtful advantage.

Another bismuth salt, 6BiOCl,Aq., or $[2(BiCl_3 \cdot Bi_2O_3)H_2O]$, is called *pearl white,* a name which has also been applied to indigo-tinted flake white.

Pigments containing antimony. *Antimony white,* antimonious oxide, Sb_4O_6, finds employment as a substitute for flake white, particularly on the Continent. In oils, especially, this pigment is durable and trustworthy. Another antimony white is *powder of algaroth*

$$Sb_4O_6 \cdot 2SbCl_3.$$

Antimony yellow, true *Naples yellow, Jaune d'Antimoine, Giallo di Napoli,* is basic lead antimoniate, PbO,Sb_2O_5, and is now usually prepared by heating together potassium antimonyl tartrate, lead nitrate and sodium chloride. The product is cooled, washed, and ground. Numerous other processes have been used. Naples yellow is fast to light, but is readily attacked by sulphuretted hydrogen, even in oil-painting; is discoloured by contact with iron and is inadmissible in conjunction with indigo and various other organic pigments, such as the yellow lakes and cochineal products. Naples yellow, or an allied antimonial yellow, has been used for many centuries in enamels and pottery ware. It is unsuitable for water-colour painting. Several imitations of this pigment are, or have been, in the market: one is a mixture of cadmium yellow with zinc white; another was a variety of yellow ochre (Church).

Antimony vermilion, antimonzinnober, antimonious sulphide, Sb_2S_3, or oxysulphide, $2Sb_2S_3,Sb_2O_3$, is a fine red pigment of satisfactory covering power, but limited application owing to its sensitiveness to dilute alkalis and acids. The methods of manufacture are based upon the interaction of the alkaline or alkaline earthy thiosulphates and antimonious chloride. An orange-coloured variety of this pigment, *antimony orange,* is made by using sulphuretted hydrogen as the precipitant.

Pigments containing arsenic. Those in which arsenic is associated with copper have already been considered. There remain the arsenic sulphides:—

King's yellow, Royal yellow, arsenic yellow, auripigmentum, orpiment, arsenic trisulphide, As_2S_3, a brilliant, but fugitive and extremely poisonous pigment, immiscible with lead, mercury, and copper compounds, and now almost entirely superseded by the chromium colours. It is prepared either by precipitation or sublimation.

Arsenic red, arsenic orange, realgar, arsenic disulphide, As_2S_2. This pigment, prepared by a fusion and sublimation-method, is also highly poisonous and generally unsuitable for artists' use.

Pigments containing tin. *Tin white,* stannic hydroxide or orthostannic acid, $Sn(OH)_4$, is used in enamel- and glass-making, but scarcely at all for ordinary decorative or artistic work. To a very considerable extent it has taken the place of bismuth subnitrate and oxycarbonate as a face-pigment.

Mosaic gold, aurum musivum or *mosaicum,* '*Bronze powder,*' stannic sulphide, SnS_2, a lustrous yellow scale-preparation, made by heating a mercury-tin amalgam together with sulphur and ammonium chloride; or a mixture of tin monosulphide, SnS, with mercuric chloride is heated. Another 'bronze' is prepared by fusing together stannic oxide and sulphur. A fused mixture of tin and bismuth, to which mercury is added before the liquid has cooled, yields a silver-tinted metallic pigment.

Other compounds of tin, such as 'tin salt' (stannous chloride, $SnCl_2$), stannic chloride, $SnCl_4$, 'pink salt,' $SnCl_4 \cdot 2NH_4Cl$, and sodium stannate, $Na_2SnO_3,3H_2O$, although not pigments, are largely used in the manufacture of the lake-colours.

Pigments containing gold. The use of finely divided metallic gold, whether in the form of leaf, or otherwise, by mediæval artists, monkish scribes, and others, in pictures and illuminated manuscripts, also in the colouring of crimson glass, is well known.

Cassius' purple, gold stannate,

$$Au_2SnO_3 \cdot SnSnO_3,4H_2O \text{ or } Au_2,3SnO_2,$$

is used in glass-ware and ceramic art.

Pigments containing aluminium. The *metal*, finely powdered, now receives a wide application as the pigmentary constituent of aluminium paint.

Kaolin, China clay, hydrated aluminium silicate, $Al_2O_3{\cdot}2SiO_2,2H_2O$, is durable and practically unalterable as a pigment. In oils, it is somewhat deficient in covering power, but in water-colour and tempera painting it is a very serviceable white pigment, and may fulfil the function of a 'filler.' Thus, a 'Chinese white,' for water-colour painting, may contain 3 parts of kaolin to 1 part of zinc oxide. The process of manufacture consists in levigating and drying the natural clay, the main impurities in which are flakes of undecomposed mica and crystals of quartz. Kaolin is much used in the manufacture of paper, and it is an inexpensive carrier for lake-pigments.

Alumina $Al_2O_3,3H_2O$, though not used as a pigment alone, is a component of many lakes, and occasionally forms part of various composite white pigments, such as satin white, *blanc fixe*, and the like.

Ultramarine, Bleu d'Outremer, one of the most permanent, trustworthy, and beautiful of pigments, was formerly obtained exclusively from the rare and costly mineral *lapis lazuli*, a variety of hauyne, by an elaborate and tedious elutriation method. The chief constituents of ultramarine are alumina, soda, silica, and sulphur. The formula is doubtful, but may be $Na_4(NaS_3Al)Al_2(SiO_4)_3$ (Brögger and Backström). In 1828, Guimet succeeded in manufacturing artificial ultramarine, a pigment little inferior to the natural product of the same composition, equally permanent both in oil and water-colour painting, and moderate in price. Several varieties of artificial ultramarine are made: sulphate ultramarine, which possesses a pale greenish-blue shade; soda ultramarine, poor in silica, the purplish-blue product most in use; and soda ultramarine, rich in silica, a pigment mostly used by paper-makers. *Lime green* or *green ultramarine* is the first stage in the manufacture, and is the colouring ingredient of green water-paints. By roasting with sulphur, green ultramarine is 'coloured,' *i.e.* it is caused to assume the azure tint. Other varieties of ultramarine than those mentioned are *red, violet*, and *yellow ultramarine*. The raw materials used in making artificial ultramarine are kaolin, silica, soda, carbon, sulphur, and sodium sulphate. *Mineral grey* and *ultramarine ash* are grey and bluish-grey residual products from the processes of treatment of the mineral *lapis lazuli*.

Ultramarine violet is obtained when the soda blue is heated with sal ammoniac for many hours at a temperature of about 150°. Further heating with steam and hydrochloric acid converts the violet pigment into *ultramarine red*.

Pigments containing iron. *Yellow ochre, mineral yellow, Roman ochre, Oxford ochre, stone yellow, brown ochre, golden ochre, Chinese yellow*, &c., are silicious and argillaceous earths, often containing as impurities lime, barium, and other metallic salts, but all owing their yellow or brown colour to the presence of hydrated ferric oxide. These colours, which are prepared for the market by careful sampling and elutriation, are mined in many parts of the world, are exceedingly lasting, have no effect upon other pigments, are not injured by light or by impure atmospheres, and they can be used with any medium. Ochres vary in opacity, as they vary in composition: most of them possess fair covering power. Pigments of this class were used by the ancient Egyptians, Assyrians, Greeks, and Romans.

Raw Sienna, Terra di Siena, Italian earth, is a browner-tinted, manganiferous yellow ochre, occurring in Tuscany, in the vicinity of Rome, Cyprus, and elsewhere. Some American siennas are of very serviceable quality. Raw sienna is fitted for oil, water-colour, tempera, and fresco-painting.

Burnt Sienna is a pigment of an orange-brown tint, permanent and suitable for every sort of artistic work. It is made by cautiously calcining raw sienna.

Red ochre, Scarlet ochre, Red chalk, Ruddle, Bole, sinopis, Terra rosa, &c., are varieties of the native anhydrous ferric oxide, or red hæmatite, Fe_2O_3. All are durable pigments and good driers.

Indian (or *Persian*) *red* is, in strictness, a native product (also hæmatite), of a somewhat purplish shade, imported from the East. But some so-called *Indian red* is manufactured by calcining ferrous sulphate (copperas, or green vitriol), $FeSO_4,7H_2O$, or by roasting yellow ochre for about 12 hours.

Light red, Burnt ochre, Brun rouge, also, is calcined yellow ochre. The period of heating is 10 hours. This pigment is an opaque, permanent, and innocuous colour, of a scarlet tint, tempered by shades of brown and grey.

Venetian red, Colcothar, Caput mortuum vitrioli, Crocus, Rouge. The natural pigment known as Venetian red is a variety of red hæmatite, of a purer red than either *light red* or *Indian red*, but the artificial products are obtained by calcining copperas, or the ochres. Time, in the case of the ochres, about 8 hours; temperature, a low red heat. If pure, Venetian red is uninjurious to other permanent colours, but soluble salts, especially sulphates and traces of acid, must be absent. The last-named exert a detrimental action upon organic pigments, such as indigo; upon the vehicle used; and also on the surface coated, if this chance to be of metal.

Prussian brown, a rarely used pigment consisting of ferric oxide in admixture with carbon and made by carefully calcining Prussian blue. It is permanent and a good drier.

Mars yellow, Mars orange, Mars red, Mars brown, and *Mars violet.* These are artificial ferruginous pigments, prepared by precipitating salts of iron, with or without the addition of alum, by milk of lime or an alkaline hydroxide, drying, and calcining the precipitates at various temperatures, according to the colour required. The Mars pigments present no particular advantages over the ordinary iron yellows and reds, and they may be somewhat injurious to certain of the madder pigments.

Terre verte, Verona green, Veronese earth, Green earth, &c., are pale, bluish-green, natural pigments, consisting essentially of an alkaline and magnesian ferrous silicate; but as the localities are numerous, considerable variations in composition are observed. *Terre verte* is one of the most inert and permanent pigments used by artists, but it is deficient in body and intensity of hue. It is available for painting in oil, water-colour, tempera and fresco.

Prussian blue, Chinese blue, Antwerp blue, Berlin blue, Paris blue, soluble blue, bronze blue, Saxon blue, &c. This pigment occurs in several forms. Commonly, it is a mixture of potassium ferric ferrocyanide, $K_2Fe_4Cy_{12}$, with ferric ferrocyanide, Fe_7Cy_{18}; but the most permanent form is ferric ferrocyanide, Fe_7Cy_{18}. Some of the varieties named, such as Antwerp blue and Paris blue, contain other ingredients and are inferior to the true Prussian blue, which is an intense colour with a slight greenish shade, is permanent, miscible with other pigments and useful both in oils and water-colour. It is not available for fresco-work or enamels. Though liable to fade in a strong light, it recovers its intensity of hue when kept in the dark for a while.

Pigments containing chromium. *Chrome yellow,* normal lead chromate, $PbCrO_4$, is a salt of a full yellow hue, prepared by a simple precipitation process. Usually, mixed or diluted chrome yellows are met with in commerce, lead sulphate, barium sulphate, or gypsum, being associated with the lead chromate: examples are $PbCrO_4{\cdot}PbSO_4$ and $PbCrO_4{\cdot}2PbSO_4$. *Cologne yellow* consists of lead chromate and sulphate, sometimes with calcium sulphate. *Paris yellow* is a mixed 'chrome' of a somewhat similar type. Other products are *primrose chrome, pale chrome, middle chrome,* and *deep chrome.* These colours are far from permanent, being sensitive to the action of sulphuretted hydrogen, darkened in admixture with sulphide pigments, and liable to change in the presence of reducing substances. For water-colours and distemper (tempera) painting, the yellow chromes are quite unsuitable. In oils, they are permissible, with certain limitations.

Zinc chrome, Citron yellow, zinc chromate, $ZnCrO_4$, is a pale yellow pigment of fairly good covering power, less used alone than for associating with Prussian blue in the production of various shades of mixed greens. The composition of this pigment is sometimes represented by the formula $3(ZnCrO_4),K_2Cr_2O_7$. Zinc chrome is not affected by sulphuretted hydrogen, and is miscible with most other pigments without deterioration. Acids, alkalis, and organic compounds attack it, the last-named having a tendency to change the colour from yellow to green.

Lemon chrome, Lemon yellow, Baryta yellow, Barium chrome, permanent yellow, yellow ultramarine, Steinbüller yellow, and *Jaune d'Outremer,* are names given to barium chromate, $BaCrO_4$, the most stable of the chromium pigments. Prepared by the double decomposition of barium chloride and potassium chromate, filtering, washing, drying, and grinding; lemon yellow is obtained as a very pale, moderately opaque, and serviceable pigment, which can be used with safety in oils and fresco. For water-colour painting it is less suitable, the yellow assuming a greenish hue under unfavourable conditions of exposure. The greatly inferior *strontian yellow,* strontium chromate, $SrCrO_4$, is not infrequently substituted for baryta yellow.

Lime chrome, calcium chromate, $CaCrO_4$, is a similar pigment of little value

Siderin yellow, basic ferric chromate, $Fe_2(CrO_4)_3$, is a somewhat pale-hued product, very stable, useful in stereochromy (water-glass painting), and of occasional application in water-colour work.

Copper chromate $CuCrO_4$ is a red salt, somewhat dull in hue, which has been proposed and actually used as a pigment, but it is fugitive and of little practical value. The equally unserviceable mercury and silver chromates have already been mentioned (*v. supra*).

Chrome red, Austrian cinnabar, Orange chrome, Derby red, Chinese red, &c., basic lead chromate, $PbCrO_4,PbO$ or $Pb_2CrO_4(OH)_2$, is an orange-scarlet pigment, made by heating normal lead chromate with a dilute solution of sodium or potassium hydroxide. The shade obtained depends upon the extent to which the reaction proceeds. Like the yellow chromes, the chrome reds are incompatible with sulphide pigments, such as cadmium yellow and ultramarine, and they are liable to turn green in the presence of reducing substances, such as oxidisable organic pigments. But, unlike the yellows, they may be used with caution in tempera work.

Chrome green, Vert de chrome, true chrome green. Prepared by (*a*) igniting ammonium dichromate, (*b*) igniting mercurous dichromate, (*c*) heating together potassium chromate and sulphur, (*d*) the ignition of a mixture of potassium dichromate, ammonium chloride, and sodium carbonate. This fine pigment is, or should be, either approximately pure, anhydrous chromium sesquioxide, Cr_2O_3, or (according to another process of manufacture) chromium phosphate, $Cr_2(PO_4)_2$. Some products are a mixture of the two compounds. The oxide pigments are of finer hue than the phosphate colours. Chrome green is one of the most permanent, generally trustworthy, and widely applicable colours used by artists.

Mixed chrome greens are mixtures of chrome yellow, barium sulphate or gypsum, and Prussian blue. These are greatly inferior to true chrome green and are unstable in the presence of sulphur, lime, alkalis, and oxidisable vegetable or animal pigments.

Viridian, Veridian, Vividian, Guignet's green, Mittler's green, Vert emeraude, hydrated chromium sesquioxide, $Cr_2O_3,2H_2O$, is prepared by calcining a mixture of crystallised boric acid with about one-third its weight of potassium dichromate, treating the residue with hot water, washing, wet-grinding, and drying. One of the most valuable pigments used in art, viridian is universally applicable, without action upon other pigments, and absolutely permanent. Though called, in France, *Vert emeraude,* it is, of course, entirely distinct from the fugitive and poisonous emerald green already described among the copper pigments.

Pigment containing nickel. *Nickel yellow* is a permanent colour, obtained by precipitating a solution of nickel sulphate with sodium phosphate, washing, drying, and igniting.

Pigments containing cobalt. *Cobalt yellow, Aureolin,* cobalto-potassium nitrite,

$$K_6Co_2(NO_2)_{12},xH_2O,$$

or sodium-potassium-cobalt nitrite,

$$K_2NaCo(NO_2)_6,H_2O,$$

is a bright yellow, durable pigment, which is without action upon other pigments, with the exception of the lakes, and is only very slowly attacked by sulphuretted hydrogen. Aureolin is permanent in water-colour, as well as in oils.

Cobalt pink, magnesia-cobalt pink, is produced when a thin paste of finely divided magnesium carbonate together with an aqueous solution of cobalt nitrate is dried, and subsequently ignited in a covered vessel at a high temperature. Strongly ignited cobaltous arsenate and phosphate are also of a pink or foxglove-red colour, inclining to violet. These pigments are sometimes known as '*cobalt red*' or '*cobalt violet.*'

Rinmann's green, Cobalt green, sometimes termed *zinc green,* cobalt zincate, CoOZnO, is a delicately shaded and artistically satisfactory pigment, of great permanence, and innocuous to other colours. The best product is obtained by drying and calcining zinc oxide, previously made into a paste with an aqueous solution of cobalt nitrate, sulphate or chloride. Another cobalt green is prepared by mixing zinc and cobalt solutions with sodium phosphate, and igniting the washed and dried precipitate. The product so obtained has a bluer tint than the true Rinmann's green.

Turquoise green, chrome-alumina cobalt oxide, is a bluish-green pigment mostly used in ceramic painting, but occasionally also in oils. It is made by heating to redness aluminium and chromium hydroxides together with cobaltous carbonate.

Cobalt blue, Thênard's blue, Leyden blue, King's blue, cobalt ultramarine, Gahn's ultramarine, azure blue, &c. Several methods are used in the production of cobalt blue. The variety of this pigment known as Wenzel's blue can be prepared by adding ammonia to a solution of cobalt chloride, mixing the precipitated and washed hydroxide with alumina, drying, and igniting; or by moistening recently precipitated aluminium hydroxide with a solution of cobalt nitrate, drying the mixture, and strongly igniting it. Another cobalt blue is made by mixing freshly precipitated and washed cobalt phosphate with newly precipitated and washed aluminium hydroxide. The mass is dried, ignited, and ground. Cobalt arsenate may be substituted for the phosphate. Also a mixture of alum and cobalt nitrate solutions may be precipitated by sodium carbonate, the precipitate being washed, dried, and ignited, as usual. It will be seen that cobalt blue may be a cobalt aluminate or a compound of the phosphate or arsenate of cobalt with alumina.

These cobalt pigments are permanent, except in the presence of ammonium sulphide. They are available in all media, including fresco, and are without action upon other pigments. The tint of the blue is slightly greenish, and in artificial light a shade of violet is perceptible. Cobalt blue is especially valuable in water-colour, for which it is somewhat more suitable than for painting in oils.

Leitch's blue, or *cyanine blue,* is a 'mixed' pigment, composed of cobalt blue and Prussian blue. It is moderately durable, but presents no very striking advantages. As Prussian blue is a constituent, this pigment cannot be used in fresco work.

Smalt, Saxon blue, cobalt-potassium silicate, is a deeply coloured glass which, in a fine state of division, was at one period much used as a pigment. Artificial ultramarine has, to a great extent, replaced it. Smalt is deficient in chromatic and covering power, but it is perfectly durable and without injurious effect upon any other pigments.

Cœruleum, Cerulean blue, Cœlinblau, Bleu céleste, cobalt stannate, is a greenish-blue, permanent, semi-opaque colour, made by igniting stannic oxide, previously moistened with a solution of cobaltous nitrate. It possesses the advantage of appearing less violet by artificial light than the other cobalt blues.

Cobalt brown results when cobaltous sulphate, ferrous sulphate, and ammonium sulphate, or ammonia alum, are very strongly heated together. Another method of manufacture is to mix ferric oxide with aluminium hydroxide and a cobaltous salt, the mixture being then ignited.

Pigments containing manganese. *Manganese green, Cassel green,* barium manganate, is made by cautiously heating a mixture of manganese nitrate or oxide with barium nitrate. Or, manganese dioxide and carbonate may be heated with barium peroxide. Another manganese green (Böttger's) is made as follows. A solution of manganese chlorate is precipitated by barium nitrate. The violet compound produced is washed, dried, mixed with barium hydroxide and carefully heated. A green mass results, which requires washing with water and further treatment.

Manganese blue. A mixture of kaolin, manganese oxide and barium nitrate, or of silica, manganese oxide and barium nitrate, ignited at a red heat, is stated to yield a blue product, available for use as a pigment. Soda ash, silica, calcium carbonate, and manganese oxide, mixed together and calcined, yield a similar product.

Manganese violet, mineral violet, permanent violet, impure manganese metaphosphate, is prepared by evaporating to dryness a mixture of solutions of phosphoric acid and manganous chloride, fusing the residue, boiling with ammonium carbonate solution, allowing the turbid liquid to stand, filtering, evaporating the filtrate to dryness, fusing the residue, pulverising it and boiling with water. The pigment separates as a fine violet precipitate, which must be collected on a filter, washed, and dried.

Raw umber, Turkey umber, Levant umber, Terra ombra, is a greenish- to yellowish-brown, silicious and ferruginous earth, containing a considerable proportion of one or other of the higher oxides of manganese, Mn_3O_4 and MnO_2. Most of the best specimens are of Cypriote origin, but many countries yield a supply of this natural pigment, which merely has to be ground, levigated, and dried at 100°. Raw umber is a permanent and justly-valued pigment. It has no injurious effect upon other stable colouring matters.

Burnt umber, Velvet brown, Chestnut brown, &c., result from the calcination of raw umber; they are equally permanent, and can be used in conjunction with all other durable pigments. The colour of burnt umber is warmer and richer than that of the raw product.

Cappagh brown, mineral brown, euchrome, is a highly manganiferous and ferruginous earth, obtained from the Cappagh mine, near Skibbereen, Ireland. When heated to 100° it loses water and assumes a fine reddish-brown hue, like that of burnt sienna. This pigment is suitable for work in oils or water-colour, and is permanent. Before grinding in oil, it should be dried at a temperature not exceeding 80°.

Caledonian brown possesses a reddish tint, altered upon ignition almost to black. This earth is composed chiefly of manganese and iron oxides and hydroxides; it is a useful and permanent colour, workable with all media. The original supplies are said to be exhausted, and a substitute is sold consisting of a mixture of Vandyke brown and burnt sienna (Church).

Manganese black, MnO_2, is the native manganese dioxide, very finely ground. It is expensive, too rapidly siccative, and without compensating advantages.

Pigments containing zinc. *Zinc white, Chinese white, snow white, flowers of zinc, Blanc de zinc, Zinkweiss*, zinc oxide, ZnO. This brilliantly white pigment (sometimes also called 'permanent white') is non-poisonous, permanent, innocuous to other pigments, and available for water-colour, tempera, fresco, and oils. In the last-named, however, it dries less satisfactorily than flake white, and with the lapse of time exhibits deficient opacity. For artists' work in water-colours, it cannot be excelled, and its use among painters generally, in enamels, mixed paints, dipping paints, combination white leads, and as a carrier for lake pigments, is rapidly extending. It is a mistake to consider that zinc white is wanting in covering or spreading power. In this respect, it can hold its own very well against white lead, than which, however, it possesses somewhat less body.

Zinc carbonate, $ZnCO_3$, has been used as a pigment, but with little success: it is inferior in opacity and tint to zinc white.

Zinc sulphide, ZnS, is somewhat rarely used alone as a pigment, because, though possessed of considerable body, it usually fails with regard to purity of tint. Moreover, as an artists' colour it is inadmissible, from its tendency to injure certain other pigments. Associated with barytes, zinc oxide, magnesia, or the like, zinc sulphide enters into the composition of numerous white pigments now upon the market, such as Orr's white or lithopone, Griffith's white, &c.

Zinc-lead white is an intimate mixture of approximately 50 p.c. of zinc oxide with 50 p.c. of lead sulphate. The process of manufacture is similar to that of sublimed white lead. The colour resembles that of corroded white lead, and cannot be described as a pure white. This pigment is largely used in house paints and for the dipping paints in which agricultural implements and the like are painted by immersion and subsequent draining.

Lithophone, lithopone, zinc-baryta white, ponolith, Griffith's white, Orr's white, Charlton white, oleum white, patent zinc white. These and other names have been applied to a number of patented pigments, the basis of which is zinc sulphide. Associated with the zinc compound in most cases is barium sulphate. Lithopone (the German name, which is now generally used) contains from 15 to 30 p.c. of zinc sulphide, according to the quality of the pigment: the best contains 30 p.c. From 7 to 10 p.c. of zinc oxide may be present, and the rest is barium sulphate. The parent of this class of pigments would seem to have been Orr's white enamel (1874). These products are of good body, considerable covering power, and undeniable efficiency as substitutes for white lead, with which they compete in purity of tint. The lithopones are unaffected by atmospheres which darken lead paint, but they cannot be mixed with lead or copper pigments. They are everywhere extensively used in the oil-cloth industry.

(*Zinc chrome* and *zinc green* have been dealt with under *Chromium* and *Cobalt pigments* respectively.)

Zinc grey is a name applied to zinc dust (true zinc grey), and to various mixed pigments consisting of zinc oxide mingled with mineral black, lamp black, or the like.

Pigments containing barium. *Permanent white, constant white, barytes white, enamel white*, barium sulphate, $BaSO_4$, occurs in nature as the mineral barytes, the purer grades of which are pulverised, levigated, dried, and ground for the colourman's use. The variety of this pigment, known as *Blanc fixe, precipitated barytes*, or *artificial barytes*, is made artificially by precipitating a solution of barium chloride, or some other soluble salt of barium, with sulphuric acid or a soluble sulphate. The artificial product is somewhat purer than the natural pigment, and possesses greater opacity, but it is wanting in covering power, and though employed in water-colour painting, under the name of permanent white, it cannot be recommended as an oil colour. It is, however, one of the most absolutely permanent and inert pigments known. Barytes has been largely used as a 'filler' or 'extender,' for white lead and other pigments.

Hamburg white, Dutch white, and *Venice white* are mixtures of barytes white and lead white.

Witherite, barium carbonate, $BaCO_3$, has very occasionally found its way into the market as a white pigment, but it mainly serves as the source from which barium chloride and other soluble barium salts are prepared.

(*Lithopone* has been described under *Zinc pigments*, and *Baryta yellow* under *Chromium pigments.*)

Pigment containing strontium. *Strontian white*, strontium sulphate, $SrSO_4$, has a very limited use as a white pigment. Its preparation from the mineral, celestine or celestite, is similar to that of permanent white from barytes. It is, perhaps, superior to barytes as a pigment, but is too costly for general use. (For *strontium yellow* v. chromium pigments.)

Pigments containing calcium. *Gypsum, Terra alba, satin white, mineral white, calcium sulphate*, $CaSO_4,2H_2O$, is obtained from the crude mineral by crushing, levigation, and drying. It is a permanent and useful pigment, innocuous to other colours and possessed of greater body than barytes. Paper stainers and papermakers use it in large quantities. The pigment known as satin white usually consists of a mixture of calcium sulphate and aluminium hydroxide, $Al_2O_3,3H_2O$. It possesses more body and covering power than gypsum alone.

Whitening, whiting, English white, Paris white, Spanish white, chalk, marble dust, Gilders' white, Kreide, Craie, calcium carbonate, $CaCO_3$. This pigment is used as a 'filler' or 'assistant' in mixed paints, but chiefly for whitewashing and in distemper work, as a painting-ground: it is permanent and can be mixed with all pigments, excepting vegetable colours, Prussian blue, emerald green, chrome yellow, and the like, which are likely to be affected adversely by alkalis. In oil, whitening is unserviceable and a bad drier.

Pigments containing magnesium. *Magnesium carbonate,* $MgCO_3$, prepared from the mineral magnesite by crushing and levigation, has sometimes been used as a pigment. It is permanent and available for admixture with other pigments, excepting such as are injured by alkalis.

Pigments containing silicon. *Pure silica,* SiO_2, ground to an impalpable powder, is useful for admixture with all pigments, excepting the silicious ochres, its principal function being that of a reinforcing or filling agent. Though inert and pre-eminently stable, it is too transparent for employment as a pigment alone. The main advantages of silica are its 'tooth,' and its absolute permanency. *Steatite, Soapstone,*

$$3MgO,4SiO_2,H_2O$$

is used to impart a glaze to some special paints.

(For *kaolin, v. Pigments containing aluminium.*)

Pigments containing, or consisting chiefly of, carbon. *Soot black, vegetable black, lampblack, smoke black, candle black, flame black, gas black, carbon black.* These widely used pigments are soots, obtained by the incomplete combustion of mineral oils, greases, and fat-oils, resins, tarry matters, and natural gas. Carbon or gas black is mostly produced in the combustion of the last-named. *Acetylene black* is an especial variety of gas black, obtained by exploding together in a cylinder acetylene gas and a limited supply of oxygen. Flame black is derived from tar, naphthalene, pitch, &c.: true lampblack is mainly from liquid raw materials. These pigments are nearly pure carbon, perfectly inert, entirely permanent, and uninjurious to all other colouring matters, with the exception of a few unstable organic compounds, liable to be decolourised by carbon. A very fine, pure lampblack is the pigmentary basis of Chinese or Indian ink.

Animal black, bone black (*Beinschwarz*), *ivory black, Paris black, sugar house black.* The first is obtained as the carbonaceous *residuum* of the destructive distillation of miscellaneous animal offal, the second in a like manner from bones, and the third is or should be produced similarly from waste ivory. Ivory black—particularly when the lime salts have been removed by digestion in hydrochloric acid—is the most intense of the black pigments: it is stated (Toch) that lampblack will make a light mark on ivory black. The animal blacks exert considerable decolourising power when associated in an aqueous medium with organic colouring matters · hence they are more advisedly used in oils than for water-colour painting. Notably hygroscopic, such pigments should be dried before being ground in oil. *Soap black* is a form of ivory black moulded into pastilles with a little gum-water.

Charcoal black, Frankfort black, German black, drop-black, blue-black, vine-black, and the like, may shortly be described as charcoals. They are made by calcining in closed vessels materials of the most diverse descriptions, and, as may be expected, vary greatly in value, quality, and cost. The finest bluish-black and velvety products are obtained from vine and beech twigs, fruit stones, coco-nut shell, grape husks, and dried wine-lees. Inferior charcoal blacks result from the charring of very many non-resinous, soft woods. Bass, willow, and maple woods, also paper mills' refuse, are among the materials employed. Drop-black is so named because it is sent into the market in the form of pear-shaped drops, into which it has been moulded with the aid of a little glue-water.

Mineral black, slate black, oil black or *black chalk,* is a brownish-black to blue-black, highly carbonaceous shale, occurring in Bavaria, Spain, Italy and elsewhere, suitable for pigmental use, after crushing and levigation or wet-grinding. *Coal blacks* are somewhat similar. In common with other carbon-pigments, mineral black dries slowly, but is possessed of great permanency. The more intense blacks, of artificial origin, are superseding the different varieties of shale- and coal-blacks.

Graphite, plumbago, or *black lead* is a dark grey to black pigment, of absolute permanence, available for use with all media, and miscible with other pigments. Nearly pure carbon, and extraordinarily inert, it is a valuable ingredient of paints used as protective coatings for metals. This application of plumbago is exemplified in the familiar stove polishes. With white pigments, graphite supplies the artist with neutral greys. Its use in the manufacture of drawing pencils need merely be mentioned here.

Prussiate black is the washed and dried carbonaceous residue, obtained as a bye-product in the manufacture of potassium ferrocyanide.

Prussian black results from the calcination of Prussian blue, is a mixture of carbon and oxide of iron, possesses a brownish shade and presents no particular advantages as a pigment.

Bistre is a brownish-black, bituminous soot, obtained chiefly from the smoke of beechwood. It is purified for use by digestion and repeated washing with boiling water, levigation, and grinding with gum-water or glycerol, or both. Bistre, which is not used in oils, is somewhat fugitive.

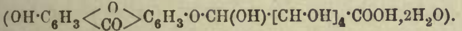
Bone brown is prepared by calcining bones until they are of a brownish colour, and grinding the product.

Vandyke brown, as generally met with in this country, is a highly bituminous, ferruginous earth. Though of a fine, rich hue, this variety of Vandyke brown is decidedly fugitive, especially in water-colour. Two other, more permanent, but far less richly-tinted pigments, sold under the same name, consist of a brown variety of *caput mortuum,* and a calcined ferruginous ochre, respectively. Imitation Vandyke browns are made, consisting of ochre, colcothar, and lampblack, in admixture.

Cassel brown, Rubens' brown, Cologne earth, Cullen earth, coal brown, and the like are, for the most part, varieties of brown coal or lignite. Some are ochreous in character and approximate in composition to the umbers. These pigments are subject to such variability of composition, that they cannot safely be trusted for artistic purposes.

Asphaltum, bitumen, mineral pitch, mummy. The use of asphalt or native bitumen, as a pigment, has been virtually abandoned by artists, but large quantities from Trinidad and elsewhere are consumed in the manufacture of varnishes, such as Brunswick black, carriage varnish, and black japan. Extreme brittleness is a disadvantageous feature of asphalt coatings. Much of the asphalt used in varnish-making is an imitative product, derived from coal-tar. The use of native bitumen by the ancient Egyptians, for embalming the dead, led to the application, in after-centuries, of the exhumed remains, ground to dust (bitumen, bones and all), as an artists' pigment, under the name of *mummy.* This colour, in an oil vehicle, is more permanent than asphaltum.

Other pigments of organic origin. *Indian yellow, Purree, Piuri, Purrea Arabica,* is composed mainly of the impure, basic magnesium salt of euxanthic acid



$$(\mathrm{OH\cdot C_6H_3}<\substack{\mathrm{O}\\ \mathrm{CO}}>\mathrm{C_6H_3\cdot O\cdot CH(OH)\cdot [CH\cdot OH]_4\cdot COOH,2H_2O}).$$

The compound is $\mathrm{Mg\cdot C_{19}H_{16}O_{11},5H_2O}$, and is excreted in the urine of cows fed upon the leaves of the mango tree, *Mangifera indica* (Linn). This pigment is exclusively made by natives of India at Monghyr, Bengal. The urine is evaporated, the yellow residue dried, collected on calico and rolled into balls, which are sold in the native bazaars. Indian yellow is moderately permanent in oils, well suited for fresco work, somewhat fugitive in water-colour, and apt to injure certain of the lakes when associated with them. It is unaffected by sulphur compounds.

Gallstone, a yellow pigment derived from a calculus formed in the gall-bladder of oxen. It has been used as a water-colour, but is of no permanence and little value.

Gamboge, gutti, gummigutt, gomme-gutte. This familiar pigment is a gum-resin yielded by Malayan, Siamese, Burmese, Indian, and Cingalese species of *Garcinia.* Gambogic or cambogic acid, the principal of the resin acids constituting the pigment, is $\mathrm{C_{30}H_{35}O_6}$ (Buchner). Gamboge is better adapted as an oil pigment than for water-colours, but even in oil it is not permanent unless beeswax, solid paraffin, or a resin such as Venice turpentine or copal be present also. As a water colour, gamboge is best avoided: alkalis darken it, and light not infrequently diminishes its brilliancy of tint. If admixed with cadmium sulphide or barium chromate, it is less alterable, but aureolin and purree are more trustworthy pigments.

Dragon's blood. The dragon-tree of the Canary Islands, *Dracœna Draco* (Linn.), the rattan tree, *Calamus draco,* and a variety of other plants, yield deep red-coloured resins known in commerce under the above name. The chief supplies appear to be obtained from *Doemonodrops draco* (Blume.), and are exported to Europe from Southern and Eastern Asia, under the name of palm dragon's blood. The main tinctorial component consists of the benzoic and benzoyl-acetic esters of dracoresinotannol, $\mathrm{C_8H_9O\cdot OH}$, associated together; the first-named being greatly in excess. Dragon's blood is mostly used as a colouring ingredient for varnishes, wood stains, French polish, and the like. As a pigment it is fugitive and untrustworthy. It dries poorly and is injured by certain other pigments, such as flake white.

Hooker's green and *Prussian green* are 'mixed' pigments, composed of gamboge and Prussian blue.

Indigo, indigotin, indigo blue, $\mathrm{C_{16}H_{10}N_2O_2}$, or $\mathrm{C_6H_4}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C:C}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C_6H_4}$, is formed by the fermentation of the glucoside, indican, $\mathrm{C_{52}H_{62}N_2O_{34}}$, a constituent of various species of *indigofera,* especially *I. tinctoria* (Linn.), and of other plants, such as woad, *Isatis tinctoria* (Linn.). Commercial indigo is impure indigotin and is greatly improved in quality and hue ('intense blue') by successive treatment with hydrochloric acid, hot water, sodium hydroxide solution and strong alcohol (Church). Synthetic indigo is now a formidable rival to the natural product, and is stated to contain 97 p.c. of the pure pigment. Indigo in oils and water is wanting in permanency, and suffers deterioration in the presence of chromes and other pigments. It is alleged, however, that there are prepared 'absolutely fast' indigo lakes (Zerr and Rübencamp, Eng. ed., 1908, translator's note, p. 450).

Sepia is the dark brownish-black pigmentary matter contained in the ink-bags of the *sepia,* or cuttlefish, and allied cephalopodous organisms. The method of preparation consists in boiling the crude sepia with caustic soda solution, filtering, precipitating the colouring matter from the alkaline solution by the addition of hydrochloric acid, collecting, washing, and drying. Sepia is permanent, inert, and suitable both for oils and aqueous media. It is especially useful for monochrome work and in water-colour painting. The exact chemical nature of the compound melanin (apparently a weak organic acid, *sepiaic acid*), which constitutes 78 p.c. of the pigment, is at present incompletely studied.

Pigments composed of lakes. The lake colours have, during the past two decades, become of prominent importance. They are fully dealt with in the article 'LAKES,' vol. iii. p. 235. In contradistinction to the pigments already described, which, for the most part, are *substantive* colours, *i.e.* consist of homogeneous particles (*e.g.* aureolin, chrome green, lampblack), the lake pigments are *adjective* products, and are compounds of a soluble, (usually) organic colouring principle with an insoluble inorganic base, most often non-pigmental, and generally, but not invariably, white. Among the bases employed are aluminium hydroxide, calcium sulphate, zinc oxide, kieselguhr, kaolin, and iron oxide, but many others are used. Three classes of lakes come within the category of pigments: (1) lakes made from animal colouring matters; (2) lakes prepared from vegetable substances; and (3) lakes obtained from coal tar products. Lakes belonging to the first two classes were in use at a very early period, but the far more numerous lakes made from artificial colouring principles are of quite modern introduction.

Carmine is the most important example of a lake pigment belonging to the first of these classes. The dried females of the cochineal insect, *Coccus cacti,* are boiled with water, alum, stannous chloride and sodium carbonate being added. After standing for a few days, the decanted liquid throws down the pigment as a crimson precipitate, which is washed and dried. Analysis shows that the major part of the inorganic base present, together with the carminic acid, $C_{22}H_{22}O_{13}$ (Liebermann), is alumina. By varying the quantity and nature of the base, other lake pigments—cochineal lakes—are produced. These contain more water and more of the aluminous or other bases than carmine. *Carmine lake* (*Florentine, Vienna, Paris* or *Munich lake*) may be regarded as little more than a variety of carmine. *Crimson lake* is more basic than either. *Purple lake* contains a lime-alumina base, and *scarlet lake* is a 'mixed' pigment, composed either of alizarin red or of crimson lake, brightened by vermilion.

Indian purple results when cochineal extract is precipitated by solution of copper sulphate.

Burnt or *roasted carmine* is obtained by cautiously heating carmine. A similar product, called *burnt lake*, can be prepared from crimson lake.

All these cochineal pigments, though beautiful in hue, are excessively fugitive, and should be excluded from the artist's palette.

Lac lake, Indian lake, lac dye lake, lack lack. A resin called gum lac is formed on *Ficus religiosa* (Linn.) and other trees, when punctured by *Coccus lacca*, an organism similar to the cochineal insect. The exudation, though initially vegetable, runs from the female insect and solidifies on the twigs as stick lac. This, extracted with water, yields lac dye, and the insoluble residue constitutes the seed lac and shellac of commerce. After purification, the lac dye (laccaic acid, $C_{16}H_{12}O_8$, Schmidt) is extracted with an alkaline solution and subsequently treated with alum. The precipitated lac lake is washed and dried. This pigment is less fugitive than the cochineal lakes, but its hue is inferior (*v.* Lac Dye).

Among the lake pigments belonging to the second class mentioned above, those prepared from vegetable substances, are the natural *madder lakes.* The madder root, *Rubia tinctorum* (Linn.), contains, together with purpurin, $C_{14}H_5O_2(OH)_2$, the glucoside ruberythric acid, $C_{26}H_{28}O_{14}$, which by hydrolysis yields dihydroxy-anthraquinone or alizarin,

$$C_{14}H_6O_2(OH)_2.$$

This compound is capable of giving, according to the nature and proportions of the bases employed in association with the acidified and washed madder root (alumina, lime-alumina, iron oxide, copper oxide, *et alia*), crimson, pink, purple, brown, and plum-coloured lakes. Under similar conditions, purpurin gives orange-hued and bright-red products. The principal natural madder pigments are *madder red, rose madder, madder carmine, pink madder, purple madder, Rubens' madder*, and *madder brown*; but these lakes from the madder root are now almost obsolete, the preparation of artificial alizarin and purpurin from anthracene, $C_{14}H_{10}$, having led to the cheap and facile production of artificial 'madder lakes' (*infra*) on a large commercial scale. Whether natural or of artificial origin, the madder pigments, although alterable by prolonged exposure, are, as a class, far less perishable than the coccus lakes. This statement does not apply to the so-called 'yellow madder,' yellow lake (next paragraph), and the like, which are extremely fugitive pigments.

Other lakes from vegetable sources are those from red sanders wood, alkanet root, *Anchusa tinctoria* (Lam.) (including the pigment called *violet carmine*), Brazilwood, logwood or campeachy wood, archil, buckthorn, and quercitron or black oak. The pigments known as *Vienna lake* and *rose pink* are prepared from Brazil wood, *Caesalpinia Braziliensis* (Linn.); *yellow lake, brown pink, Italian pink, 'yellow madder,' Dutch pink, yellow carmine, citrine lake, 'stil de grain,' sap green, lokao* (*Chinese green*), and other pigments, are derived from quercitron bark, *Quercus discolor* (Ait.), &c., or from different species of buckthorn (*Rhamnus*), including Persian, Avignon and other berries. Violet, blue, red, and intense blue-black lakes can be prepared from logwood. *Hæmatoxylon compechianum* (Linn.). French purple is an archil lake. Red and violet lakes are yielded by red sanders or santal wood, *Pterocarpus santalinus* (Linn.). All these pigments are fugitive and untrustworthy. Old fustic, *Chlorophora tinctoria* (Gaudich), young fustic, *Rhus Cotinus* (Linn.), and turmeric, *Curcuma tinctoria*, may be mentioned here, but they are dye-woods, rather than sources of pigments (*v.* separate articles).

There remain to be considered the lakes obtained from coal-tar products. These, to a great extent, have superseded the lakes of animal and vegetable origin. They have already been described in the article 'Lakes' to which reference may be made. The following short list includes only some of the important groups, and the names of a few of the more familiar pigments: Group 1. *Alizarin or artificial madder lakes* (previously mentioned); the names of some of the pigments have already been given, but the commercial designations of other representative examples are *alizarin orange* (*marigold, pure yellow*), *alizarin carmine, permanent crimson, olive green, olive lake, sap green, Indian lake, scarlet lake, alizarin pink, alizarin blue*, and *alizarin violet.* Group 2. *The triphenylmethane*, $CH(C_6H_5)_3$, *or rosaniline group of lakes*: *e.g.* the magenta and violet lakes. Group 3. *Lakes from the halogen-substituted phenol-phthaleins, or eosins*; *e.g.* '*vermilionettes*,' *Victoria reds, Royal reds*, &c. Group 4. *Lakes from the amino-phthaleins or rhodamines*: *e.g.* deep pink to bluish-red lakes. Group 5. *Lakes from sulphonated azo compounds*; exceedingly numerous, and ranging in colour from various shades of yellow to deep violet-reds. Group 6. *The azine, oxyazine, and thioazine lakes*: e.g. *Nile blue A, methylene blue B*; also various red lakes.

Unfortunately, the pigments obtained from the artificial colouring matters, with the exception of the alizarin lakes and some of the pigments produced from the azo colours, are neither light-fast nor are they damp-fast or air-fast. Many of the most brilliant products are deteriorated by a few hours' exposure. Apart from the artificial madder lakes, practically all these exquisite pigments are useless to the artist.

Stability. For many years past much attention has been devoted to the subject of the permanency or stability of pigments under various conditions. The agencies to which the painter's colours may ordinarily be subjected are light, air (possibly in association with varying quantities of noxious gases, such as sulphuretted hydrogen and sulphur dioxide), moisture, the vehicle or medium used, the associated pigments, and, in some cases, the painting ground.

As long ago as 1772, Sir Joshua Reynolds tested some of the pigments he used, and since his time many observers have similarly experimented, but in a more systematic and scientific manner: among them, Dyckman, Andrew, Decaux, Simpson, Rood, Hartley, Russell and Abney, Church and Laurie. Much good work in this connection has been done by the Munich Deutsche Gesellschaft für Beförderung rationeller Malverfahren; and during the years 1894–1904, the Burlington Fine Arts Club carried out a series of valuable tests of water-colour paints, exposed to light under different conditions. Ogden N. Rood, whose experiments were made with washes of several dozen water-colours upon drawing-paper during three and a half summer months' exposure, found only the following twelve pigments unaffected: yellow ochre, Roman ochre, cadmium yellow, Indian red, light red, *jaune de Mars*, cobalt, smalt, French blue, burnt sienna, burnt umber, and terre verte. The experiments of Russell and Abney, upon the action of light on water-colours, showed that when washes upon Whatman paper were exposed for nearly two years to light and air, the following pigments remained unchanged: Indian red, Venetian red, burnt sienna, chrome yellow, lemon yellow, raw sienna, terre verte, chromium oxide, Prussian blue, cobalt blue, French blue and ultramarine ash. In the table below, the approximate order of instability of the pigments, the most fugitive being placed first, is set forth:—

1.*Carmine
2.*Crimson lake
3.*Purple madder
4.*Scarlet lake
5.*Payne's grey
6.*Naples yellow
7.*Olive green
8.*Indigo
9.*Brown madder
10.*Gamboge
11.*Vandyke brown
12.*Brown pink
13.*Indian yellow
14. Cadmium yellow
15. Leitch's blue
16.*Violet carmine
17.*Purple carmine
18.*Sepia
19. Aureolin
20. Rose madder
21. Permanent blue
22. Antwerp blue
23. Madder lake
24. Vermilion
25. Emerald-green
26. Burnt umber
27. Yellow ochre
28. Indian red
29. Venetian red
30. Burnt sienna
31. Chrome yellow
32. Lemon yellow
33. Raw sienna
34. Terre verte
35. Chromium oxide
36. Prussian blue
37. Cobalt blue
38. French blue
39. Ultramarine ash

The colours marked with an asterisk altered during only four months' exposure; Nos. 27 to 39 showed no change during two years. Of thirty-four mixtures, only three remained unaltered at the end of the period; but six mixtures containing Prussian blue, though changed at first, returned more or less to their original colour when kept in the dark for six weeks. Prussian blue, which has suffered in tint from exposure to sunlight, is well known to possess the remarkable property of recovering its colour when placed in darkness. Among Russell and Abney's conclusions were: (1) that mineral colours are far more stable than vegetable pigments; (2) that moisture and oxygen are essential for changes to be effected in vegetable colours; (3) that in a mixture of colours having no direct chemical action on one another, light causes the unstable colour to fade, leaving the stable pigment virtually unaltered; and (4) that the more refrangible rays of light, which produce the greatest change in pigments, are present in comparatively small proportion in the lights usually employed in illuminating a room or picture-gallery.

The German society above-mentioned selected the following list of *normal colours* for oil-painting, as having been shown by experience to be the most permanent and trustworthy under the influences of light and air: white lead, zinc white, Naples yellow, cadmium yellow (darker shades), Indian yellow, brown and yellow ochre, terra di siena, burnt ochre, red ferric oxide colours, vermilion, madder (alizarin) lake, cobalt blue and green, ultramarine, the Prussian blues, chromium oxide green, green earth, umber, asphalt, mummy, ivory black and lampblack (Zerr and Rübencamp).

The Burlington Fine Arts Club trials, which were made with washes of a considerable number of moist water-colours upon Whatman paper exposed to dry air, moist air, and in glazed frames, respectively, were totally unfavourable to gamboge, Indian yellow, Vandyke brown, crimson lake and vermilion; but it was proved that Prussian blue, indigo, sepia and other pigments liable to change in damp air, may be regarded as tolerably stable if so framed as to be kept dry.

As the outcome of many experiments of his own and a consideration of the results obtained by other observers, Church concluded that, for oil-painting, the following pigments are truly permanent:—

Flake white
Zinc white
Baryta white
Yellow ochre
Raw sienna
Naples yellow
Cadmium yellow
Cadmium orange
Red ochre
Venetian red
Light red
Indian red
Vermilion
Cobalt violet
Manganese violet
Emerald oxide of chromium
Green oxide of chromium
Green ultramarine
Cobalt green
Ultramarine { natural
  artificial
Cobalt
Cœruleum
Burnt sienna
Raw and burnt umber
Verona brown
Cappagh brown
Prussian brown
Ivory black
Charcoal black
Lamp black
Graphite

Generally allowable, though liable to some alteration in special circumstances, are—

Baryta yellow
Strontia yellow
Chrome yellow
Aureolin
Indian yellow
Rose madder
Purple madder
Rubens' madder
Madder red
,, carmine
Mars violet
Emerald green
Madder green
Malachite green
Terre verte
Smalt
Prussian blue
Antwerp ,,
Madder brown
Vandyke brown (earthy)
Cologne earth
Bitumen

And the pigments named below, in Church's opinion, should not be used in artistic painting—

Yellow madder
Brown pink
Yellow lake
Gamboge
King's yellow
Zinc chromate
Carmine and burnt carmine
Crimson lake
Indian lake
Purple ,,
Scarlet ,,
Violet carmine
Sap green
Verdigris
Green vermilion, etc.
Indigo
Blue verditer
Blue ochre
Vandyke brown (bituminous)

For water-colour and tempera painting, flake white, pale cadmium, true Naples yellow, chrome yellow, artificial vermilion, malachite green, madder brown, bistre, and sepia, must be added to this last list as being quite untrustworthy. Other pigments, in addition to the foregoing, are unsuitable for fresco work and stereochromy e.g. the Prussian blues, Antwerp blue, all the chromates and the madder colours.

The pigments regarded by Decaux as quite unchangeable in oils are: zinc white, flake white, yellow ochre, Naples yellow, deep cadmium, raw sienna, red ochre, Mars red, Venetian red, burnt Italian earth, green oxide of chromium, terre verte, green ultramarine, artificial ultramarine, cobalt blue, and ivory black.

With reference to the action of foul gases, it may be stated generally that the lead and copper pigments are especially sensitive to sulphuretted hydrogen; the chromates of zinc and barium are liable to turn green in the presence of sulphur dioxide; ammoniacal vapours will injuriously affect the copper greens and Prussian blues; acid fumes may injure ultramarine, and reducing or oxidising gases attack indigo.

Certain pigments should not be used in conjunction: thus, aureolin and indigo, aureolin and cochineal lakes, cadmium yellow and emerald green, vermilion and malachite, white lead and lithopone, and chrome yellow and lithopone, are examples of mixtures, the components of which may mutually react when intimately mixed. In an oil medium, there is less likelihood of such injurious interaction than with water-colour pigments, but it may be affirmed that it is in general wiser to mix pigments on the palette than to grind them together. E. G. C.

PILOCARPENE, PILOCARPIDINE, PILOCARPINE *v.* JABORANDI.

PILOLITE *v.* ASBESTOS.

PIMARIC ACID *v.* RESINS.

PIMELIC ACID $C_7H_{12}O_4$. Twenty-five isomeric acids having this formula have been prepared, and of these three are known as *pimelic acid.*

Normal pimelic acid $CO_2H[CH_2]_5CO_2H$, obtained by the oxidation of fats (Bouveault, Bull. Soc. chim. 1898 [iii.] 19, 562), and of castor oil (Gantter and Hell, Ber. 1884, 2213); prepared by the oxidation of suberone (*v.* suberic acid) with nitric acid (Schorlemmer and Dale, Annalen, 199, 147); by heating pentanetetracarboxylic acid at 200°–220° (Perkin and Prentice, Chem. Soc. Trans. 1891, 825); by treating αε-dichloro-, dibromo-, or di-iodopentane with potassium cyanide and hydrolysing the nitrile thus formed (Braun, Ber. 1904, 3588; Hamonet, Compt. rend. 1904, 139, 59); by the interaction of the sodium compound of ethylcyanacetate and trimethylene dibromide (Carpenter and Perkin, Chem. Soc. Trans. 1899, 924); by the interaction of piperidine, cyanogen bromide, and phosphorus pentachloride (Braun, Chem. Zentr. 1909, ii. 1993); by the action of sodium in amyl alcohol on salicylic acid (Einhorn and Wilstätter, Ber. 1894, 33; Einhorn and Lumsden, Annalen, 286, 260; Walker and Lumsden, Chem. Soc. Trans. 1901, 1198); by the reduction of furonic acid with hydriodic acid and red phosphorus (Baeyer, Ber. 1877, 1358); by the reduction of piperylene dicarboxylic acid with sodium in alkaline solution (Willstätter, Ber. 1898, 1550); by the interaction of trimethylene bromide and malonic ester and heating the product thus formed (Perkin, *ibid.* 1884, 3289). Crystallises in needles from benzene and plates from water; m.p. 105°. By heating the acid with lime, *cyclo*hexanone is produced. Substituted alkyl pimelic acids are produced by the reduction of substituted *o*-phenol carboxylic acids (Einhorn, Annalen, 295, 173; Chem. Zentr. 1897, i. 1006; D. R. P 90556).

β-pimelic acid is identical wth *normal pimelic acid.*

Pimelic acid, iso-*Propylsuccinic acid*—

$$(CH_3)_2CH{\cdot}CH(CO_2H){\cdot}CH_2CO_2H$$

prepared by fusing *d*-camphoric acid with caustic alkali (Hlasiwetz and Grabowski, Annalen, 145, 207; Mahla and Tiemann, Ber. 1895, 2152; Crossley and Perkin, Chem. Soc. Trans. 1898, 22); by the action of nitric acid on *β-iso*propyl-δ-ketohexoic acid (Crossley, Chem. Soc. Trans. 1902, 676); by the action of potassium permanganate on tetrahydrocarvone in alkaline solution (Baeyer and Oehler, Ber. 1896, 36); by treating amylene bromide with potassium cyanide and hydrolysing the resulting nitrile (Auwers and Mayer, Annalen, 298, 150 and 177); by similarly treating *iso*caprolactone (Blaise, Compt. rend. 124, 90); by the reduction of teraconic acid, dimethyl-4-citraconic acid, or -mesaconic acid with sodium amalgam (Fittig and Krafft, Annalen, 304, 206); by treating *iso*thujone with potassium permanganate and sodium hypobromite (Wallach, Ber. 1897, 423). M.p. 116°–117° (Bentley, Perkin, and Thorpe, Chem. Soc. Trans. 1896, 274); readily soluble in chloroform, benzene, and warm water. Oxidation with potassium dichromate and sulphuric acid converts it into terebic acid, $C_7H_{10}O_4$ (Lawrence, Chem. Soc. Trans. 1899, 527).

γ-Pimelic acid, β-methyladipic acid—

$$CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CO_2H.$$

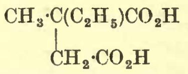
This acid contains an asymmetric carbon atom, and hence exists in two stereoisomeric forms.

d-Acid, prepared by the oxidation of citronellal or citronellic acid (Tiemann and Schmidt, Ber. 1896, 908; Semmler, *ibid.* 1893, 2257), of *iso*pulegol (T. and S., *ibid.* 1897, 25), of pulegone (Semmler, *ibid.* 1892, 3516), or of menthone (Manasse and Rupe, *ibid.* 1894, 908). Can be obtained from menthol (Beckmann and Mehrländer, Annalen, 289, 378). Melts at 93°–94·5° (Wagner, Ber. 1894, 1642), at 84·5° (Semmler, *l.c.*).

l-Acid, prepared by the oxidation of *l*-citronellal (T. & S. Ber. 1896, 923), m.p. 84·5°.

Inactive acid. Prepared by the oxidation of *i*- citronellal (T. & S. *ibid.* 1896, 925) or from equal quantities of the *d*- and *l*- acids: m.p. 93°–94°.

iso*Pimelic acid, αα-methylethylsuccinic acid*



$$\begin{array}{l} CH_3{\cdot}C(C_2H_5)CO_2H \\ \quad | \\ \quad CH_2{\cdot}CO_2H \end{array}$$

prepared from amylene bromide and potassium cyanide (Hell, Ber. 1891, 1390; Bauer and Schuler, J. 1878, 733), or from the mixture of tricarboxylic acid esters (b.p. 135°–160° at 0·15 mm.), obtained by treating ethyl α-bromomethylethyl acetate with sodiomalonic ester in xylene solution (Auwers and Fritzweiler, Annalen, 298, 166; 292, 154, and 182): m.p. 103°–104°.

PIMENTHOL *v.* CAMPHORS.

PIMENTO. Pimento or Allspice is the dried, full-grown but unripe fruit of *Pimenta officinalis* (Lindl.).

The plant is indigenous to the West Indies and is largely cultivated in Jamaica, whence our supplies are derived. The globular berries, dark purple when fresh, brown when dry, are from 5 to 8 mm. in diameter. They are enclosed in a two- but sometimes one- or three-celled fruit. They are gathered when of full size but still not quite ripe, and dried in the sun.

The characteristic flavour is due to an aromatic, pungent, volatile oil, resembling in smell that of cloves; other important constituents being a fixed oil, tannin, resin, and much starch. Full analyses by Richardson (U. S. Dept. of Agric., Div. of Chem. Bull. 13, 221) yielded the following results:—

	Whole	Ground Max.	Ground Min.
Water	6·19	8·82	5·51
Ash	4·01	5·53	3·45
Volatile oil . . .	5·15	3·32	2·07
Fixed oil . . .	6·15	6·92	3·77
Fibre	14·83	18·98	13·45
Proteid	4·38	5·42	4·03
Nitrogen	0·70	0·87	0·64
Quercitannic acid ('tannin equivalent') . .	10·97	12·74	8·27

Uses. Pimento finds its chief use as a condiment, but it is *officinal* in the British Pharmacopœia together with an *aqua* and the essential oil. Its therapeutic action is that of an aromatic stimulant and carminative.

Adulteration. Comparatively little is sold in the ground state in this country, so that pimento is rarely if ever adulterated here. Very few samples, however, are examined under the Sale of Food and Drugs Acts. The usual spice adulterants may be looked for, namely, added starches, ground olive stones, and the shells of coconut and almond, &c.

Analysis. Microscopical examination will suffice to detect all the likely adulterants of vegetable origin. The most characteristic structures to be observed are minute starch grains, usually about 8μ in diameter and not exceeding 12μ, with a distinct hilum, often joined in pairs or triplets, or larger aggregates; numerous colourless stone cells, some very large; and pigment cells containing irregular port wine or amber-coloured masses of resin or gum.

The most useful determinations are ash, tannin, and fixed ether extract. Unless adulteration is discovered by the microscope, anything further is seldom required. Should olive stones or nutmeg be suspected of being present, their special characters are given under Pepper (*q.v.*).

The direct determination of tannin is neither easy nor satisfactory, but very fair results may be obtained by calculating the quercitannic acid from the proportion of oxygen absorbed from potassium permanganate.

The process, due to Richardson (U. S. Dept. of Agric., Div. of Chem. 13, 167), is as follows: Boil 2 grms. of the sample, after thoroughly extracting with ether, with 300 c.c. of water for 2 hours, cool, make up to 500 c.c. with water and filter. Mix 25 c.c. of the filtrate with 750 c.c. of water, add 25 c.c. of indigo solution (made by dissolving 6 grms. of potassium sulphindigotate in hot water, cooling, adding 50 c.c. of sulphuric acid (conc.) and making up to 1 litre). Then titrate with the permanganate solution (1·333 grms. per litre) until the liquid becomes of a bright yellow colour. Note the number of c.c. used. Ascertain the equivalent of the permanganate in terms of N/10 oxalic acid and calculate the number of c.c. of the former used in oxidising the pimento solution. Convert this into its equivalent number of c.c. of oxalic acid. Each c.c. of the oxalic acid =0·0623 grm. of quercitannic acid.

The following table will afford some idea of the figures yielded by genuine samples, but comparatively few analyses of authentic specimens are on record.

Analyses by Winton, Ogden and Mitchell, Ann. Rep. Connect. Agricult. Station, 1898, p. 204.

	Max.	Min.	Average
Moisture . . .	10·14	9·45	9·78
Ash	4·76	4·15	4·47
,, soluble in water .	2·69	2·29	2·47
,, insol. HCl . .	0·06	0·00	0·03
Ether extract, volatile .	5·21	3·38	4·05
,, ,, fixed .	7·72	4·35	5·84
Alcohol extract . .	14·27	7·39	11·79
Starch (diastase method) .	3·76	1·82	3·04
Fibre	23·98	20·46	22·39
N.	1·02	0·83	0·92
Quercitannic acid . .	12·48	8·06	9·71

Standards. The United States standard for Allspice provides that the quercitannic acid shall not be less than 8 p.c., the ash not more than 6 p.c., the ash insoluble in HCl not more than 0·5 p.c. and the fibre (which should be determined as in pepper) (*q.v.*) not more than 25 p.c. C. H. C.

PIMENTO OIL *v.* Oils, Essential.

PINACHROMY and **PINATYPE.** Processes of colour photography devised by E. Koenig (*v.* J. Soc. Chem. Ind. 1906, 657).

PINCHBECK. An alloy of zinc and copper brought into notice by Christopher Pinchbeck in the latter part of last century. It was formerly much employed in the making of watch-cases, and other small ornamental articles in imitation of gold. Its composition is variable, but usually consists of 9 parts of copper to 1 part zinc.

PINE-APPLE. The fruit of *Ananas sativus* (Schult.) [*Bromelia ananas*] a tropical plant, grown largely in the West Indies, Singapore, Florida, the Bahamas, Natal, and other hot countries. According to Munson and Tolman (J. Amer. Chem. Soc. 1903, 25, [iii.] 272), the average composition (38 samples) of fresh pine-apples, 21 from Florida, 10 from Cuba, 4 from Porto Rico, 2 from the Bahamas, and 1 from Jamaica, is

Water	Protein	Free acid (asH_2SO_4)	Reducing sugar	Cane sugar	Ash	Insoluble matter
85·83	0·42	0·60	3·91	7·59	0·40	1·52

In different specimens, the reducing sugars varied from 1·76 to 9·75 p.c.; the cane sugar from 3·0 to 10·5 p.c. According to Lindet (Bull. Soc. chim. 1884, 40, 65), pine-apples contain 1 p.c. or more of mannitol. Pine-apple juice is said to contain an enzyme, *bromelin*, which resembles pepsin and can digest a thousand times its weight of proteids in a few hours. It can be precipitated from the juice by the addition of common salt, and can operate in acid, neutral or alkaline media (J. Franklin Inst. 1902, 154, [iv.] 262). The leaves of the plant furnish a fibre which can be used for the manufacture of rope, being stronger than flax. It is also used in the Philippines for the preparation of a cloth (Board of Trade Journal, Dec. 1898, 671; also Bull. Imp. Inst. 1904, 2, 168). Pine-apples are often canned, being preserved in their own saccharine juice, with or without the addition of sugar. Analyses of commercial samples by Munson and Tolman (*l.c.*) gave the following average figures:—

	Water	Protein	Free acid	Reducing sugar	Cane sugar	Ash	Insol. mat.
I. Singapore	86·73	0·46	0·42	8·00	5·40	0·39	1·37
II. Singapore	81·83	0·41	0·32	11·63	5·14	0·40	1·44
III. Singapore and Straits	78·97	0·46	0·26	9·91	7·77	0·27	1·14
IV. Bahamas	85·87	0·33	0·56	7·96	2·78	0·38	1·39

I. average of 10 samples known to be preserved in their own juice; II. preserved with addition of cane sugar; III. and IV. commercial samples, III. apparently containing added sugar, IV. probably without added sugar.

The flavour of pine-apples can be imitated by a solution of ethyl butyrate in alcohol (Hofman, Annalen, 81, 87). H. I.

PINE-NEEDLE OIL *v.* OILS, ESSENTIAL.

PINE OIL *v.* OILS, ESSENTIAL.

PINE RESIN *v.* RESINS.

PINUS SYLVESTRIS OIL *v.* OILS, ESSENTIAL.

PIPE-CLAY *v.* CLAY.

PIPERAZINE (*Ethylene-imine*; *Diethylene-diamine*), also known as *Dispermine* or *Arthriticine* $(C_2H_4NH)_2$, was first obtained pure by Magert and Schmidt in 1890.

Ammonia is allowed to act upon ethylene bromide or chloride when a mixture of bases is formed consisting of ethylene- and triethylene-diamine, diethylene- and tetraethylene-triamine and diethylene diamine. The last-named is separated from the other salts by treating the mixture with excess of sodium or potassium nitrite and heating to 60°-70°. Dinitrosopiperazine, m.p. 154°, separates as a scaly crystalline mass readily soluble in hot water. The nitroso compound on being treated with concentrated acids or reducing agents yields ammonia and salts of piperazine from which the pure base is obtained by distillation with alkalis.

Piperazine and its salts are also manufactured by treating dinitroso-diphenyl piperazine with 40 p.c. aqueous solution of an acid sulphite or with hydrochloric, sulphuric, or phosphoric acids. The mixture is heated to boiling, when a violent reaction takes place, and the dinitroso-compound dissolves to a yellow liquid. When the reaction is over, the product is acidified with hydrochloric acid and the amino-phenol-sulphonic acid which separates is filtered off. The filtrate is now made alkaline and the piperazine is distilled off with steam. It is purified by conversion into its hydrochloride and the piperazine is isolated by the decomposition of the latter (Eng. Pat. 5320, 4497; J. Soc. Chem. Ind. 1893, 463; *ibid.* 1894, 275). It is also obtained by the reduction of ethylene oxamide with zinc dust or sodium (D. R. P. 66461); by heating disulphone piperazides with sulphuric acid at 200°-250° and subsequently treating the product so obtained with powdered sodium hydroxide (Eng. Pat. 7120; J. Soc. Chem. Ind. 1893, 545; D. R. P. 100232); by the decomposition of dibenzyl-piperazine with dilute sulphuric acid at 100° (D. R. P. 98031; Chem. Zentr. 1898, ii. 743); by heating sodium ethylene glycollate with acid derivatives of ethylene diamines at 250°-350° (D. R. P. 67811), and by heating α- or β- dinaphthyl piperazine with acids or with solutions of calcium or zinc chloride (D. R. P. 79121). For other methods of preparing piperazine, compare D. R. PP. 73354, 70055; 70056; 73125; 74628; 60547; 63618; 65347; 71576; 77351; 83524; 59222.

Properties. Piperazine forms lustrous glassy tablets, m.p. 104°; b.p. 140°-145°; readily soluble in water but less so in alcohol. It is very hygroscopic, forming a sesquihydrate, $C_4H_{10}N_2,6H_2O$, m.p. 44°, b.p. 125°-130°, which, on distillation above 135°, yields the pure anhydrous base (Berthelot, Compt. rend. 1899, 129, 687; *see* also Magert and Schmidt, Chem. Soc. Proc. 1893, 35).

Piperazine readily absorbs carbon dioxide, forming the compound $C_5H_{10}N_2O_2$ (Rosdalsky, J. pr. Chem. 1896, [ii.] 53, 19). Piperazine is a strong base forming crystalline salts with acids of the type $C_4H_{10}N_2, 2A$ (Herz, Ber. 1897, 30, 1584). Its aqueous solution is precipitated by mercuric chloride, Nessler's solution, copper sulphate, picric acid, potassium bismuth iodide, and by gold and platinic chlorides. It also combines with bismuth chloride (Vanino and Hartl, Arch. Pharm. 244, 216). In its chemical and physical properties it is very similar to spermine with which it was at one time thought to be identical. Piperazine is readily oxidised by potassium permanganate in the cold; it is non-poisonous and has no caustic action, and owing to the ease with which it forms a readily soluble urate, it is employed in gout and similar manifestations of uric acid diathesis (Riesenthal, Virchow's Archiv. 137, 51; Ber. 1891, 24, 241; 1897, 30, 1584). It is also used for the relief of irritation of the bladder due to excess of uric acid in the urine. Piperazine can be identified in urine by its characteristic lemon yellow picrate (Riesenthal, Chem. Zentr. 1893, ii. 624) or by adding a slight excess of caustic soda, heating the solution, cooling, and filtering. The filtrate is acidified with hydrochloric acid and potassium bismuth iodide is added when a brick red precipitate consisting of characteristic microscopic crystals separates.

Piperazine is best preserved in a solution of 20 parts alcohol and 80 parts water. Like piperidine, piperazine reacts with isatin, forming blue additive compounds (Liebermann and Kraus, Ber. 1907, 40, 2492). It also forms additive compounds with quinols and phenols (Stevignon, Bull. Soc. chim. 1910, [iv.] 7, 922) and with aldehydes, carbon disulphide and carbonyl chloride (Herz, *l.c.*).

Piperazine combines with diiodo-, or dibromo-pentane when they are heated together on the water-bath forming diethylene dipiperidyl halide (Braun, Ber. 1907, 40, 2935).

n-**Dibromopiperazine** is obtained by the action of hypobromous acid on piperazine and treating the product with dilute alkali or piperazine. It forms yellow, transparent short prisms which, without melting, are dangerously explosive at 79°–80°. It readily combines with two molecules of hypobromous acid to form a comparatively stable additive compound which explodes at 72° without melting (Chattaway and Lewis, Chem. Soc. Trans. 1905, 951). Periodides have been obtained by Linarix, J. Pharm. Chim. 1909, [vi.] 30, 241.

α-2 : 5-**Dimethyl piperazine**, m.p. 118°–119°, b.p. 162°, is formed by the reduction of 2 : 5 dimethyl pyrazine or of lactimide with sodium and alcohol (Hayer, Zeitsch. physiol. Chem. 34, 347); or it is isolated from commercial amyl alcohol by treating it with sodium (Bamberger and Einhorn, Ber. 1897, 30, 226). It is alkaline, readily soluble in water and in alcohol, and sublimes at ordinary temperature. The *β*-compound has m.p. 114°–115°, b.p. 162°.

α-**Dimethylpiperazine tartrate** or **Lycetol**, $C_6H_{14}N_2{\cdot}C_4H_6O_2$, m.p. 250°, is a white crystalline powder having an acid reaction. It is readily soluble in water, is less hygroscopic than piperazine, and its solution is more stable than that of the latter. It also has a more agreeable taste than piperazine itself.

Piperazine benzoate, glistening plates, subliming at 120°, and the **salicylate**, fine white needles subliming at 160°, are formed by mixing alcoholic solutions of the base and acid. The former is alkaline and the latter neutral to helianthin but both are acid to phenolphthalein (Astruc, Bull. Soc. chim. 1906, [iii.] 35, 169). They can also be formed by fusing the two substances together and recrystallising from the above solvent (Eng. Pat. 25905; J. Soc. Chem. Ind. 1897, 933; Pharm. Zeit. 43, 319).

The **tartarate** and **citrate** (Eng. Pat. 26078; J. Soc. Chem. Ind. 1898, 68) which are non-hygroscopic and may be dried at a high temperature, and also the **quinate** (Eng. Pat. 11420; J. Soc. Chem. Ind. 1899, 856) are produced similarly. Piperazine also forms acid salts with oxalic, tartaric and citric acids which yield useful neutral double salts with lithium (Eng. Pat. 18981; J. Soc. Chem. Ind. 1896, 758).

Piperazine mercuric citrate is formed by mixing together piperazine and mercuric citrate in absolute alcohol. It crystallises in white needles sintering at 110°, m.p. 137°, and forms a strongly alkaline solution in water.

Piperazine mercuric acetate is formed similarly, is fairly soluble in water, darkens at 188° and has m.p. 198°.

Both these salts, as also the corresponding mercuric-*sulphate-cyanide* (m.p. 144°–145°) *-benzoate* (m.p. 107°–108°) *-salicylate* and *nitrate* and also the corresponding *diethylpiperzaine mercuric nitrate* (m.p. 148°–151°), *-sulphate* (m.p. 124°–125°), *cyanide* (m.p. 159°–160°), *-succinate* (m.p. 108°–110°) and *-salicylate* (m.p. 128°–130°) have antiseptic properties and do not coagulate albumen. They can also be prepared by treating the mercuric salt with the carbonate of the organic base (D. R. P. 125095, 1902).

Piperazine theophylline is formed by combining molecular proportions of its components or their salts. It has an alkaline reaction, is sparingly soluble in alcohol but readily so in water (D. R. PP. 214376, 217620, 224981; J. Soc. Chem. Ind. 1910, 1134).

Piperazine cinchonate or **sidonal**,

$$C_4H_{10}N_2(C_7H_{12}O_6)_2,$$

m.p. 168°–171°, is a colourless crystalline powder having an acid taste and reaction and is readily soluble in water (Pharm. Zeit. 45, 182).

α-**Piperazine anthraquinone**, formed by the action of nitroanthraquinone on the base, separates from methyl alcohol in orange-red crystals (D. R. PP. 136777, 136778, 1903).

Nitrosopiperazine $C_4H_8N_2(NO)_2$ formed by adding sodium nitrite to a solution of piperazine hydrochloride and warming the mixture; it crystallises from water in yellowish lustrous plates, m.p. 158°, and gives the Liebermann reaction with phenol and sulphuric acid.

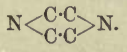
Diphenyl piperazine, m.p. 163·5°, is formed by the action of ethylene bromide on aniline, sufficient dry sodium carbonate or acetate being added to fix the hydrogen bromide produced. It combines with a number of diazo and diazosulphonic compounds yielding yellow-red and violet dyes for cotton, wool, and silk (Bischoff, Ber. 1889, 22, 1777).

Piperazine forms phosphates and arsenates of the type $C_4H_{10}N_2,H_3PO_4,H_2O$;

$$C_4H_{10}N_2,2H_3PO_4$$

(Astruc and Brenta, Bull. Soc. chim. 1908, [iv.] 3, 963), and also glycero- phosphates (Astruc, Compt. rend. 1905, 140, 727).

A large number of other piperazine derivatives have been prepared (Ladenburg, Ber. 1891, 24, 2400; Bischoff and Nastvogel, *ibid.* 1889, 22, 1783, 1792; Bischoff and Trapesonzjanz, *ibid.* 1892, 25, 2940; Wolff, *ibid.* 1893, 26, 721; Herz, *l.c.*; Stoehr, J. pr. Chem. [ii.] 47, 439; *ibid.* 48, 191; Cazeneuve and Moreau, Compt. rend. 1897, 125, 1182; *ibid.* 1898, 126, 1802; Rijn, Chem. Zentr. 1898, i. 380; Knorr, Ber. 1904, 37, 3507; *ibid.* 1905, 38, 3136; *ibid.* 1906, 39, 1420; Astruc, Bull. Soc. chim. 1905, [iii.] 33, 839; Borsche and Titsingh, Ber. 1907, 40, 5008; Van Dorp, Rec. trav. chim. 1909, 28, 18; Franchimont, *ibid.* 1910, [ii.] 14, 296).

Piperazines are the derivatives of the ring  $\mathrm{N}\!<\!\begin{matrix}\mathrm{C{\cdot}C}\\ \mathrm{C{\cdot}C}\end{matrix}\!>\!\mathrm{N}$. They are formed by the methods given above and also by the reduction of the corresponding pyrazines with sodium and alcohol. They form strong colourless bases, some liquid and some crystalline; they fume slightly in air and readily absorb carbon dioxide. The piperazines form hydrates which are readily soluble in alcohol or chloroform but sparingly soluble in water. The poly-substituted pyrazines always give 2 isomeric piperazines on reduction. The lower piperazines have higher boiling-points than the corresponding pyrazines whilst for the higher compounds this relation is reversed (Stöhr, J. pr. Chem., 1897, [ii.] 55, 49).

PIPERIC ACID *v.* RESINS.

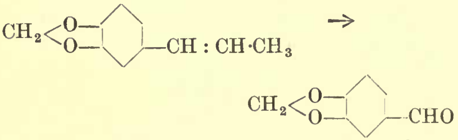
PIPERIDIN *v.* RESINS.

PIPERIDINE *v.* BONE OIL.

PIPERIDINE GUIACOLATE *v.* BONE OIL.

PIPERINE *v.* RESINS; also VEGETO-ALKALOIDS.

PIPERONAL (*Heliotropine*) methylene-protocatechuic aldehyde, $CH_2O_2 : C_6H_3{\cdot}CHO$, was first obtained by Fittig and Mielk (Annalen, 1869, 152, 35) by the oxidation of piperinic acid, and its constitution was established by Fittig and Remsen (*ibid.* 1871, 159, 158). It is closely connected with various natural products including piperine, safrol and *iso*safrol, from all of which it may be obtained on oxidation. Piperonal itself occurs only to a limited extent in nature, being generally found in conjunction with vanillin and other alkyl-oxyaldehydes; it is found in small quantities in spiraea oil and also in certain vanilla fruits such as the vanillon or pompona (Göller, Chemist and Druggist, 1907, 65, 13). It has not been proved whether the characteristic smell of the flowers of the heliotrope variety, from which the commercial name is derived, is actually due to this compound. Piperonal, although not used in the preparation of scents and essences, is employed considerably for the purpose of soap perfumery and is now prepared in large quantities, especially by Schimmel and Co., by the oxidation of *iso*safrol (Bericht von Schimmel & Co., April, 1893).



Otto and Verley have proposed to obtain piperonal by the action of ozone on safrol or *iso*safrol (D. R. P. 97620).

Properties and reactions.—White crystals, m.p. 37°, b.p. 263°, very slightly soluble in water, easily so in most organic solvents. With dilute hydrochloric acid, protocatechuic aldehyde is formed and carbon is said to be liberated. According to Schut (Chem. Zentr. 1910, i. 1829), the reaction is much more complicated; with phosphorus pentachloride there is formed piperonal chloride $CCl_2O_2 : C_6H_3 \cdot CHO$; with sulphur chloride the reaction proceeds more smoothly; with water this compound yields quantitatively protocatechuic aldehyde, so that this is a satisfactory method of preparation from piperonal (Schimmel & Co., D. R. P. 165727); with sodium amalgam there is formed piperonyl alcohol and two isomeric hydropiperoins; aniline condenses to form piperonal anilide; ammonium sulphide forms dithiopiperonal; acid sodium sulphite forms an addition compound, as also does trinitrobenzene. By condensation with α-bromopropionic ester, piperonal may be converted into an acid which loses carbon dioxide, forming *iso*safrol (Wallach, Annalen, 1897, 357, 72).

PISANGCERYLIC ACID $C_{23}H_{47}COOH$, m.p. 71°, is obtained from Pisang wax.

PISANG WAX *v.* Waxes.

PISOLITE *v.* Aragonite.

PISTACHIA LENTISCUS *v.* Sumach.

PITCH. Various substances met with in the organic kingdom when submitted to destructive distillation yield, in addition to fluid products, a residuum that on cooling assumes a more or less viscous or solid character: and, furthermore, at various places on the earth's surface extensive deposits are found consisting of black, resinous substances of similar appearance and properties. To these products have been assigned the terms of 'pitch,' 'bitumen,' and 'asphaltum.' Each of these substances possesses distinctive features, and each in its place fulfils important requirements in the arts.

Bitumen, asphaltum, mineral pitch. These compounds consist of complex mixtures of hydrocarbons, and are found in many localities and under the most varied conditions. Probably the celebrated Pitch lake, situated in the island of Trinidad, and said to be upwards of three miles in circumference, represents one of the most important deposits of natural bitumen known, although within the past forty years many additional sources have been found in Cuba, Central and South America, California, Arkansas, Nicaragua, and Peru, in India, Palestine, Egypt, Turkey, Italy, France, Germany, Switzerland, Ho-Tsing, province of Szu-Tehuan, China, and Asiatic Russia.

The origin of these deposits is involved in considerable obscurity; they appear to have been formed by the oxidation of the unsaturated hydrocarbons in petroleum. Bitumen has been regarded either as a product of chemical action or as a distillate produced by natural causes from animal and vegetable remains. It has been argued that if the bitumen were the result of a purely chemical process, we should expect to find a generic uniformity in the character of the substance wherever found on the earth. On the other hand, if petroleum is the result of metamorphism, its generation is co-existent only with that of metamorphic actions. If we accept this hypothesis, the generation of petroleum must be considered as practically ended.

In studying the asphalt of Bentheim, Patrono, Castro, Colla San Magna, and other places, the conclusions arrived at have confirmed the views of Mendeleeff to the effect that their formation has been brought about by inorganic means. Bitumen is frequently met with in places where, from a geological point of view, its occurrence can be explained only by assuming that it has accumulated within the fissures in the same manner as that contained in lavatic geodes, and separated from prehistorical tufaceous deposits by inorganic means. Engler, who has given some considerable study to the Bentheim asphalt, furnishes the following particulars respecting it. It is insoluble in alcohol, ether, carbon disulphide, oil of turpentine, and similar solvents, but melts when strongly heated: sp.gr. 1·092. It contains:

	I.	II.
Carbon . . .	89·46	89·83
Hydrogen . .	9·55	9·88
Ash . . .	1·09	1·14

Distillation yielded the following products:—

	I.	II.
Tar	36·8	38
Coke	48·9	48
Gas and water . .	14·3	14

The tar obtained by the distillation of the asphalt on a large scale was free from phenol and creosotic compounds, and the products of its distillation were as follows:

	p.c.
Burning oils	12·72
Gas and lubricating oils . .	9·78
Paraffin	1·50
Paraffin grease . . .	0·65
Coke from retorts . . .	46·09
Coke from tar . . .	0·86
Pitch	1·52
Loss, gas and water . .	26·88
	100·00

Egyptian asphalt contains :

	p.c.
Carbon	85·29
Hydrogen	8·24
Oxygen	6·22
Nitrogen	0·25

The bitumen of Judea, found floating on the Dead Sea, contains :

	p.c.
Carbon	77·84
Hydrogen	8·93
Oxygen	11·54
Nitrogen	1·70

Sulphur is invariably present in natural bitumens, varying in quantity from 3 to 4·2 p.c. and even 10 p.c. ; from such samples, hydrogen sulphide is always given off on heating. Asphaltums and bitumens vary considerably in character. Generally, their appearance is that of smooth, hard, brittle, black, or brownish-black resin, breaking with a distinct conchoidal fracture : the sp.gr. varies from 1 to 1·7 ; when free from mineral matter they may be even lighter than water. When distilled with water, asphaltum yields a volatile oil called by Boussingault 'petrolene,' probably consisting of a mixture of paraffins. The residue of 'asphaltine,' which remains when the petrolene is completely driven off, is a solid black substance resembling the original substance prior to distillation, but which does not soften below under about 300°, and decomposes below its fusing point.

Trinidad pitch yields, when heated—

	p.c.
Volatile organic matter . .	76·75
Non-volatile organic matter .	17·77
Ash	5·48
	100·00

Natural bitumen is only partially soluble in alcohol, but more completely so in carbon disulphide, carbon tetrachloride, petroleum spirit, chloroform, oil of turpentine, coal-tar, benzene and naphthas ; the pyridine bases, also derived from coal-tar, scarcely act upon it. The portion, however, that passes into solution communicates a strong greenish fluorescence to the liquid, and when examined spectroscopically, in the manner described for examining crude anthracenes for certain impurities (Chem. News, 26, 199 ; 31, 35, 45), two distinct absorption bands are visible near the D line of the spectrum, from yellow to green, which distinguishes it from all other pitches, coal-tar excepted, which occasionally shows bands, but invariably situated in the blue portion of the spectrum near the F and G lines.

In petroleum spirit, 74·23 p.c. of its organic matter is soluble and 20·29 p.c. insoluble.

At a temperature varying from 58° to 60° bitumen softens, and it melts at about 100°, although varieties are met with that melt only at a much higher temperature.

The following table of results obtained by A. E. Jordan and given in Allen's Organic Analyses shows the difference between natural asphalts and artificial products.

Material.	Ash.	Organic matter.		Action of petroleum spirit.		
		Volatile.	Non-volatile.	Soluble.	Insoluble.	Percentage of organic matter soluble.
Asphalt (origin unknown) .	0·60	80·79	18·61	47·63	51·77	47·91
Trinidad pitch . . .	5·48	76·75	17·77	74·23	20·29	78·53
Petroleum pitch	none	50·43	49·57	36·16	63·84	36·16
Shale oil pitch	0·25	66·40	33·35	63·62	36·13	68·77
Coal-tar pitch	0·15	49.33	50.52	18.56	81.29	18·58
Bone pitch (inferior) . .	0·33	56·15	43·52	29·96	69·71	30·05

Boussingault's methods are not now used and the terms petrolene and asphaltene used by him have received another significance, that portion soluble in petroleum spirit, ether, or acetone being known as petrolene and the portion insoluble in any of these liquids but dissolved by boiling turpentine or cold chloroform being known as asphaltene.

Applications of asphaltum.— The purer asphaltums are employed almost exclusively for the manufacture of black varnishes and japans, for which purpose they are eminently adapted, yielding surfaces and coatings of great brilliancy and not prone to 'break up' or disintegrate. Asphaltum selected for the purpose of the varnish maker should be practically free from mineral matter or within a limit of 5 p.c., it should be completely soluble in carbon disulphide, chloroform, high boiling coal-tar naphtha, and oil of turpentine (mineral matter excepted). It should break with a conchoidal fracture and brilliant lustre. It should not flow or lose shape, like wood tar and many of the fatty pitches, when left on a plane surface, and an angular fragment should retain its shape and the sharpness of its angles in boiling water.

Asphalt rock. Asphaltum is often met associated with sand or limestone or the two variously admixed ; in this condition the mineral is known as 'asphalt rock,' and occurs in the upper Jurassic formation interstratified with ordinary limestone.

The following figures, by Durant Claye, show the proximate composition of some rock asphalts employed for paving :—

	Val de Travers Switzerland.	Lobsann Alsace	Seyssel Ain France	Maestu Spain	Ragusa Sicily
Water and other matters volatilised at 100° C.	0·35	3·40	0·40	0·40	0·80
Bituminous matter	8·70	11·90	9·10	8·80	8·85
Sulphur in organic combination or free state	0·08	4·99	—	trace	—
Iron pyrites	0·21	4·44	—	—	—
Alumina and oxide of iron	0·30	1·25	0·05	4·35	0·90
Magnesia	0·10	0·15	0·05	3·85	0·45
Lime	49·50	38·90	50·50	5·70	49·00
Carbon dioxide	40·16	31·92	39·80	8·15	39·40
Combined silica	—	—	—	11·35	—
Sand	0·60	3·05	0·10	57·40	0·06
	100·00	100·00	100·00	100·00	100·00

Native calcareous asphalt exhibits a brown or nearly black colour and breaks without evidence of cleavage. The fracture is earthy and granular, not unlike chocolate, both in appearance and colour. When long exposed to the air it loses this character and then resembles ordinary limestone: this change, however, only extends to the surface.

The specific gravity of rock asphalt is about 2·23. It is hard and may be broken with a hammer, but when warmed it may be softened to a kind of paste and at about 60° falls to powder.

Good rock asphalt is homogeneous in structure and shows no indication of contained limestone. It is frequently veined, and contains large crystals of calcite impregnated with bitumen; this feature is considered an important indication, bad specimens or low qualities showing an absence of such impregnation, which renders them difficult to manipulate. Val de Travers, Seyssel, and other asphalt rocks, when employed for paving, are melted with definite proportions of good native material, such as Trinidad pitch. The product of this mixture is technically known as 'mastic,' and in using it further additions of bitumen, shale oil, and grit are frequently made.

The following analysis by Durant Claye will convey a general idea of these compositions:

	Refined bitumen from Bastennes	Imitation asphalt made from coal-tar
Moisture	0·30	0·60
Bituminous matters soluble in carbon disulphide	69·35	20·65
Organic matter insoluble in carbon disulphide	4·40	18·45
Alumina and oxide of iron	2·85	2·65
Magnesium and calcium carbonates	2·65	39·60
Silica	20·35	18·05
	100·00	100·00

For determining the actual bituminous matter in asphaltic rocks, natural and otherwise, the air-dried sample is exhausted with suitable solvents, which may consist of carbon disulphide, Russian oil of turpentine or coal-tar benzene. The operation may be conducted in a Soxhlet's tube, and if a correction be made for the moisture expelled at 100° the loss of weight furnishes the quantity of bitumen removed. The determination may be further checked by distilling off the solvent and weighing the residue, observing the usual precaution of drying at 100° until constant. The bitumen thus obtained should be heated further to 220°, when, if the sample is good, there will be little or no further loss of weight; if, however, volatile oils or petroleum be present, the loss may be considerable.

The volatile oil is best determined by repeatedly digesting the powdered sample with cold alcohol and weighing the residue; the exhaustion may be considered as complete when a portion of the alcoholic washing shows no turbidity on dilution with water.

If the residue left after exhaustion exhibits a dark colour, other organic constituents of valueless nature are present. Their proportion may be ascertained by igniting the weighed residue left after the removal of the bitumen, re-carbonating it with ammonium carbonate, again gently igniting it and re-weighing. The loss of weight represents the quantity of non-bituminous matter present.

Val de Travers asphalt gives up the whole of its organic matter to petroleum spirit, imparting a deep brown colour to the fluid, perfectly free from fluorescence, whereas the soluble portion of coal-tar pitch does not exceed 20 or 25 p.c., yielding a solution exhibiting a deep greenish fluorescence, a characteristic of this pitch in any of its solvents and which renders its detection alone or in admixture a matter of no great difficulty (*v. infra*).

Pitches derived from technical processes.

Artificial pitches. Coal-tar pitch may be looked upon as occupying the most prominent position in the series, both as regards the magnitude of its production and its corresponding consumption for the purposes of artificial fuel, asphalts and varnishes.

Some idea of the extent to which this residue is produced in the United Kingdom, together with the industry springing out of it, may be gathered from the statement that according to the last census of production the total output of tar for the United Kingdom was 846,000 tons, representing according to the same authority 647,000 tons of pitch, by far the larger proportion of which is consumed in the manufacture of patent fuel.

Coal-tar pitch is the residue remaining in the stills after separation of the various fractions known as naphthas, light oils, carbolic, creosote and anthracene oils, and amounts to about two-thirds of the weight of the tar operated upon. Its physical character is mainly dependent upon the temperature employed in distillation; but its ultimate chemical composition is more or less governed by the quality and composition of the coal distilled. It may be either 'soft' or 'hard' or 'medium'; it may be either 'normal,' as a product resulting from the simple distillation of tar, or it may be otherwise, as when mixed with green or other tar oils before running from the stills. The selection of tar distillates to be used in thus thinning down a pitch carried to a full limit of distillation is important, as it has been found that when creosote or naphthalene is employed, a pitch is obtained lacking in binding or cementing power, and blocks or briquettes made from it are liable to crumble. This defect is only obviated by the use of the heavier distillates, such as green oils which are of a more viscid and adhesive character.

When pitch is passed through a red-hot tube it yields about 250 times its bulk of gases, chiefly hydrogen.

Pitch may be utilised by burning it into lamp-black, and, according to Thenius, 500 kilos. of pitch yield 200 kilos. of varying descriptions of lamp-black and 200 kilos. of coked residue.

Referring more generally to the several results that may be obtained by varying the fractions during the distillation of coal-tar, it may be stated that if the operation be terminated at the point at which the light oils only are driven off, the residue in the still, representing about 80 p.c. of the charge, may be used for the preparation of asphalts, under the name of 'refined' or 'prepared' tar, although it is very doubtful whether material of this character is to be met with in the present day. If about 10 p.c. more is run off, the residue is soft pitch; moderately hard and hard pitch follow, the latter when the distillation is carried on as far as practicable in wrought-iron stills. The 'asphalt prepared' or 'refined tar' thus obtained by simply distilling off the naphthas and light oils, invariably contained all the constituents of the distillate that would follow if carried to its limit and collected apart, *i.e.* creosote oils, phenols, naphthalene, anthracene and higher boiling-point substances. Coal-tar pitch in its normal condition and as originally obtained, is a bright, black, lustrous substance, breaking with a well-marked conchoidal fracture; but as now met with it presents a more or less dull or greyish tint, due to the altered condition under which it is obtained. These are, firstly, distillation, in which steam, either superheated or otherwise, is injected into the still during the operation, and by which it can be pushed to a greater limit and more complete extraction of anthracene, without endangering the still; and, secondly, the admixture of the residual pitch with 'green' or other oils, in order to bring it to a consistency at which it may be run off with facility and yield a product that shall represent 'soft' 'medium,' or 'hard' pitch at will.

The proximate composition of coal-tar pitch is by no means well understood. It invariably contains some of the higher boiling hydrocarbons of coal-tar, notably anthracene, phenanthrene, pyrene, chrysene, together with bitumen and free carbon. The ultimate percentage composition of coal-tar is given by Habets as:

	p.c.
Carbon	75·32
Hydrogen	8·19
Oxygen	16·06
Ash	0·43
	100·00

Small proportions of sulphur and nitrogen are also present, the former to the extent of 0·4–0·7 p.c. Treated successively with cold benzene, carbon disulphide, boiling benzene, and boiling alcohol, Behrens obtained 23·54 p.c. of a black powder resembling anthracite and containing 91–92 p.c. of carbon, 3·1 p.c. of hydrogen, and 0·4–0·9 p.c. of ash.

Donath and Asriel (Chem. Zentr. 1903 i. 1099) give the following figures:—

——	C	H	N	S	Extract with			Residue
					Petroleum spirit	Benzene	CS_2	
Soft pitch	91·80	4·62	?	?	25·05	44·98	6·57	22·82
Medium pitch	94·32	3·98	0·148	0·77	15·14	40·03	7·10	38·16
Hard pitch	93·16	4·36	?	?	15·51	39·46	5·21	29·39

The extractions with benzene and carbon disulphide followed in rotation.

The specific gravity of hard pitch varies from 1·475 to 1·300. It is wholly insoluble in water but partially soluble in alcohol and more so in benzene or carbon disulphide. Cold petroleum spirit exerts but little solvent action upon it, but when heated it dissolves it to the extent of 18 to 23 p.c. The pyridine bases also dissolve the soluble organic matter from pitch, but somewhat tardily, and only with the assistance of heat.

Solutions of coal-tar pitch exhibit a deep yellow or yellowish-green fluorescence, which is highly characteristic of that substance. When heated it exhales an odour equally characteristic and not easily mistaken for any other known pitch. The proportion of volatile organic matter given off on heating ranges from 46 to 64 p.c.

A benzene solution of coal-tar pitch when examined spectroscopically shows a cutting out of the blue and violet portions of the spectrum, with occasional absorption bands between the F and G lines.

Testing of pitch. For the requirements of commerce, pitch has to be tested for its 'softening' and 'melting' point, and contract notes stipulate that a sample is to 'twist' fairly after immersion for two minutes in water at 60° but not under 50°, must contain at least 53 p.c. of 'volatile organic matter,' and must be free from any extraneous matter such as grit or sand.

The twisting and melting-point of pitch are ascertained by methods of comparative simplicity, only varying in trifling points and details. Probably the simplest and most readily followed is that of F. G. Holmes and is conducted in the following manner:

Several pieces of pitch are selected from different parts of the sample and cut to the size of half-inch cubes. These cubes are then supported on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 c.c. of water heated by any convenient means, at a uniform rate of 5° per minute, as indicated by a thermometer immersed in the water with the bulb about two inches from the bottom of the vessel.

The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises the pieces of pitch are removed from time to time and twisted or squeezed with the fingers and the temperature noted at which they assume the following conditions:

(1) Readily twisting or soft, *i.e.* when the pitch can be easily twisted round several times.

(2) Very soft, *i.e.* when it yields to a very light pressure of the finger.

(3) Fused, *i.e.* when the pitch melts off the wire.

Soft pitch softens at 40° and melts at about 60°.

Moderately hard pitch softens at 60° and melts at about 80°.

Hard pitch softens at 80° and melts at about 120°.

The estimation of the volatile matter is conducted in the same way as in the case of coal and other bituminous substances, viz. by heating about 1 gram of the pitch to be examined in a platinum crucible of 1¼ to 1½ inches height with the cover on, which should have a small aperture in the centre. The heat is applied by means of a good Bunsen burner, first gently until no more smoke and vapour issue from the opening in the lid, finally as strongly as the burner will permit. The operation may last 20 minutes. The crucible is then placed in a desiccator and, after cooling, the residual coke is weighed; it ranges from 36 to 53 p.c. Fixed carbon and coke dust may be determined by successively exhausting with benzene, carbon disulphide, and alcohol, employing a Soxhlet tube for the extraction.

Methods for testing the softening point of pitch have been described by Muck (Z. f. Berg. Hutten u. Salinenwesen, 1889); Schewk zu Schweinsberg (Zeitsch. angew. Chem. 1890, 704); Mabery and Sieplein (J. Amer. Chem. Soc. 1901, 20, 16); Kraemer and Sarnow (Chem. Ind. 1903, 55).

The suitability of a pitch for the purpose of artificial fuel may be ascertained by carefully distilling a given quantity of the sample in a glass retort and noting the character of the distillates; when creosote or naphthalene have been used in thinning or diluting before running from the still they are accompanied with a considerable sublimate of naphthalene passing over at a comparatively low temperature; green oils do not yield naphthalene in this manner or sublimates that may be mistaken for it.

J. E. Mills (Bulletin 343, U. S. Geological Survey), gives the following tests employed at the U. S. Government fuel testing works, St. Louis, for the testing of briquette pitch.

1. The material is distilled; all coming over below 270° is rejected as valueless. 2. The flowing point is determined by placing about 3 c.c. of pitch in the bottom of a test tube ½-inch in diameter and inserting it in a bath. The temperature of the bath is raised until, on taking out the tube and inverting it, the pitch flows 1 inch down the tube in 15 seconds. This point should be not less than 70°. 3. The pitch is extracted with CS_2. The smaller the amount of residual carbon the more satisfactory the pitch. The higher the flowing point the better the briquettes stand in the fire.

Applications and uses of coal-tar pitch. Coal-tar pitch is extensively used in the manufacture of patent or artificial fuel, varnishes, japans, and asphalts, the trade in the first-named product having assumed enormous proportions. Fuel of this description consists of admixtures of coal-tar pitch with small coal or slack, compressed into the form of blocks and known under the name of 'briquettes.' This industry would seem to be due to Ferrand and Marsais who, in 1832, obtained a French patent for using coal-tar for this purpose.

Marsais, since 1842, employed soft pitch, and in that year commenced the works at Berardy, near Saint Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The manufactured fuel was sold in that country under the name of 'peras.' The manufacture of patent fuel has opened up wide channels for the consumption not only of the immense quantities of 'slack' obtained wherever mining operations for coal are carried on, but for the almost equally large bulk of pitch resulting from the operations of the tar distiller.

This industry has developed considerably as the following figures for the output in the year 1909, taken from the Government reports, show:—

Production of Briquettes in 1909.

Austro Hungary .	117,599	metric tons
Belgium . . .	2,707,390	,,
France . . .	3,061,300	,,
Germany (Brown coal included) . .	18,748,713	,,
United States . .	126,700	,,
United Kingdom .	1,511,645	Eng. tons

In the manufacture of briquettes, certain conditions are observed, regulating shape, dimensions, and weight. The form should be that of a parallelopipedon, and they should not weigh more than 22 lbs.; they should possess a firmness approaching that of natural coal, and to attain this end the proportions of pitch used in their fabrication must be at least 5–7 p.c. They should not yield more than from 6·5 to 6·75 p.c. of ash, if intended for locomotive use, or 10 p.c. if for steamboat use.

When broken they should fracture with a clean, bright, and granular surface in the absence of which they are generally faulty. Their regular shape permits of facilities of stowage, and the loss in transit by disintegration does not amount to more than 1 or 2 p.c. against 30–50 p.c. as with coals. They should not fall to pieces in the fire but agglomerate into a firm compact coke.

Patent fuel of good quality is said to yield 10 p.c. more heating power than steam coal; it makes less dirt and when manufactured from hard pitch gives less black smoke than most kinds of coal.

In the preparation of artificial fuel of this character numerous attempts have been made to employ fatty, oily, mucilaginous, and similar substances or coal-tar, as the agglomerating or cementing medium, but the only materials now used are soft or hard pitch derived from coal-tar.

The operation of blending is comparatively simple, requiring little plant beyond that of melting pans or pug mills. Occasionally, when hard pitch is employed, a mixture of this material with coal, both in fine powder, is subjected to the action of superheated steam, by which the compound is softened and yields a compact conglomerate on cooling.

In shaping or forming such mixtures of coal and pitch into blocks or briquettes, presses with open and closed moulds are in use. The process scarcely requires description, being quite analogous to that of moulding bricks, the machine that works with dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies).

Black varnishes and japans. In the preparation of varnishes, japans, and paints for coating and protecting the surfaces of iron and wood, tar pitch is simply dissolved in, or melted with, a suitable coal-tar distillate, depending on the purpose to which the product is to be applied and the rate at which it is required to dry or become hard. These solvents vary from the more volatile benzene to the heavier xylenes or solvent naphthas, and it is not an unusual thing to employ naphthas and light oils as run from the still, up to actual creosote. No special knowledge or plant is requisite in compounding them beyond that well known to varnish makers.

As a rule the pitch should be melted at the lowest temperature, and the solvent in the first instance added in small quantities, after which it may be introduced more freely up to the desired consistency. Rosin, in varying proportions, is occasionally added, but in the majority of cases pitch alone is used. Varnishes, so prepared, will obviously vary in character, drying quality, and lustre, and it is hardly necessary to point out that when required of a nature that shall dry rapidly and with a bright uniform surface both the pitch and the solvent employed should be free from water.

Tar varnishes dry with a bright, hard surface, and adhere both to wood and iron with considerable tenacity. They have been extensively employed for coating the hulls of iron ships as anti-fouling compositions and for the purposes of protective paints generally.

Asphalts and compounds for paving. Asphalt prepared from substances derived from coal-tar has found a wide application, especially for the purpose of street paving; surfaces of ground coated or covered with asphalt become impenetrable to moisture and the passage of noxious effluvia. Coal-tar asphalt may be regarded as a soft pitch to which body or firmness has been imparted by incorporating sand, grit, gravel, chalk, lime, and substances of a similar character. The soft pitch used for this purpose may consist of the residue from tar after distilling off the more volatile constituents, and known as refined or prepared tar; or it may consist of hard pitch, afterwards melted and thinned down to the required consistency with heavy tar oils, preferably green oils.

The manufacture of this pitch into asphalt suitable for street paving is carried on in various ways. Occasionally the pitch is melted in iron pans and the ingredients to be incorporated simply added and well stirred in the mixture which contains 20–30 p.c. of pitch, and is used while hot and in a plastic condition.

Asphalt, in the form of blocks or slabs, is manufactured for similar purposes, melted pitch being run direct into a pug mill in which it is incorporated with the proper proportion of sand, gravel, or grit, and from this mill the mixture is run direct into sand moulds to harden and solidify.

Tar asphalt is said to be considerably improved by the addition of about 5 p.c. of sulphur, added in small portions at a time during the heating or melting. Much sulphuretted hydrogen is given off, and it is thought that during the heating the sulphur decomposes the constituents rich in hydrogen and thus renders the residue less fusible. Starting with soft pitch or viscid tar, it is said that 75 p.c. may be obtained as a good asphalt, which does not soften in boiling water.

Coal-tar asphalt, or more correctly, very soft pitch, is also employed for constructing 'asphalt pipes.' This industry was introduced by Jaloreau and has been fully described by Behrens (Dingl. poly. J. 208, 377). Endless hemp paper, 7 feet wide, is passed through a semi-cylindrical pan set in a furnace and filled with hot pitch. A roller revolving in the pan takes up the paper saturated with pitch and conveys it to a similar roller forming the core of the pipe, round which any number of layers of paper may be wound. When the desired thickness has been attained, fine sand is dusted on and the cylinder is exposed to considerable pressure. After cooling in water the core is withdrawn and the pipe becomes ready for use. Pipes manufactured in this manner resist very considerable pressure from within. They possess many features of value for special uses and are employed for conveying water, acids, air-blasts for pit ventilation, and for conveying underground telegraph wires.

A tarred or asphalt paper is also manufactured for packing purposes, consisting of wrapping paper impregnated with soft pitch. Another description which has been used for papering damp walls consists of two layers of paper united by a coating of pitch.

A further and more important application of materials, such as paper and felts, saturated with 'prepared or refined tar,' or pitch let down to the required consistency by solution in heavy tar oils, is for the purpose of 'roofing paper or felt.' A considerable quantity of this material is manufactured in Germany and elsewhere.

Owing to the introduction of motor vehicles, the question of reducing the nuisance caused by dust on the roads has become very important and much attention has been directed upon it. It has been found that roads made with soft pitch or prepared tar as a binder not only are less dusty but are more durable and cost less for repairs, maintenance and cleansing. Several patented articles for use as road binding agents have been put on the market, most of which consist essentially of soft pitch. This outlet has an important bearing on the pitch industry, as if a large proportion of the tar produced in the country is used for road making the output of pitch available for briquetting and other purposes will be very materially reduced.

Pitches derived from the distillation of fatty substances.

'*Stearine*' and '*palm pitches.*' Several pitches of this character are met with in commerce, notably those known as 'stearine' or 'cotton oil,' 'wool oil,' and 'palm pitch'; the two first-named representing residues from substances consisting mainly of stearic, the third of palmitic acid. Their manner of preparation is as follows:

In the purification of crude cotton seed oil by caustic soda, a more or less viscid residue is obtained, known as 'foots' or 'mucilage,' which consists largely of stearic acid in the form of an imperfectly formed soap. This material constitutes an article well known in Hull, Liverpool, London, and other centres of cotton oil refining, which has been extensively dealt with for the recovery of its 'stearine' and pitch. The soapy mucilage thus obtained in the first instance is heated in suitable vessels and then gradually decomposed by the addition of dilute sulphuric acid. This treatment separates the 'fatty acids' or 'stearine' in the form of a perfectly black greasy substance, technically known as 'black grease,' which may vary in quantity from a few p.c. to 80 p.c.

The recovery of 'stearine' and stearine pitch follows as a second step in the operation, and consists in submitting the 'black grease' so obtained to a process of distillation by the aid of superheated steam, giving the following yield:—

Inferior oils . . .	6 p.c.
'Stearine'	39 ,,
Pitch	50 ,,
Loss	5 ,,
	100

The pitch thus obtained and constituting the larger portion of the operation, may be 'hard' or 'soft,' varying with the point to which the distillation has been carried. Both are produced and met with in commerce as meeting the requirements of their respective consumers and present the following characters:

Soft stearine pitch, a viscid treacly substance, and hard stearine pitch, a firm, bright, black product, breaking with a well-marked conchoidal fracture. The sp.gr. of this pitch is about 1·35. At 55° it softens sufficiently to twist in the manner referred to under coal-tar pitch, and at 95° to 100° it melts. It is almost completely soluble in benzene and the pyridine bases, but to a much lesser degree in petroleum spirit. To this solvent stearine pitch only gives up about 71 p.c. of its organic matter, 23 p.c. remaining insoluble. Sulphur is present to the extent of 0·04 to 0·06 p.c.

It yields 79 p.c. of volatile organic matter and 21 p.c. of coke, containing 5–6 p.c. of mineral matter or ash. During the operation of heating and burning off a strong, fatty odour is evolved which at once indicates its origin and nature as an oil pitch.

A benzene solution exhibits no bloom or fluorescence, and when examined spectroscopically a cutting out of the blue or violet portions of the spectrum only: no absorption bands are visible. Stearine pitch has been extensively used for the preparation of special black varnishes used in coating tarpaulins and in various compounds employed for electrical insulation. For these requirements it is eminently adapted from the fact of yielding surfaces and combinations both supple and pliant, and that do not crack and disintegrate in the manner of some mineral pitches.

Wool-oil pitch. In the scouring and washing of woollen goods, soapy liquors are obtained in considerable quantity. These liquors are now treated for the fatty substances contained in them. The process followed is in many ways analogous to that already described, the fatty acids being separated by heating and addition of dilute sulphuric acid. On submitting these fatty acids to a similar process of distillation, an excellent stearine is recovered with a similar residue of pitch. This pitch may be hard or soft, and in both stages resembles that known as cotton or stearine pitch; it has similar uses and applications. The softer kinds are used as lubricants for heavy machinery under the name of 'hot and cold neck grease.'

Palm oil pitch. This pitch, which is now produced in considerable quantity, is the residue of an operation extensively carried out more or less in accordance with an important patent granted to Wilson and Gwynne in the year 1843, in which oils or other fatty substances were heated with sulphuric acid in place of an alkali for separation of their contained fatty acids.

In the operation claimed, the glycerol is converted into 'sulphoglyceric acid,' which is afterwards washed out, and the resultant black mass distilled with superheated steam. The respective fatty acids pass over in a condition of great purity and suitability for the various purposes applied. With palm oil, palmitic acid distils over, and palm pitch remains in the still.

In appearance and when soft, this pitch varies from those already described. It is dull in colour, with a waxy feel, but when hard is tolerably bright and black in colour, breaking with a distinct conchoidal fracture and small granular surface, but exhibiting the same waxy feel: its sp.gr. varies from 1·045 to 1·050. The softer kind twists at the ordinary temperature; the harder at 30°, although it does not completely melt under 95°. It yields about 80 p.c. of volatile organic matter and 20 p.c. of a light porous coke, containing 6·5 to 6·8 p.c. of ash. During heating a powerful fatty odour is given off, betraying its nature as being also of fatty origin. It is almost wholly soluble in benzene, but scarcely acted upon by the pyridine bases or petroleum spirit. A solution examined spectroscopically shows a cutting out of the violet portions of the spectrum but no absorption bands.

Palm pitch has been extensively used for tarpaulin varnishes, and in combination with paraffin wax, for various electrical insulators. The softer kinds are employed as hot and cold neck greases for heavy machinery.

Bone oil pitch. In the dry distillation of bones and other animal substances, an oil is obtained exhibiting a strong fœtid odour and known as bone or 'Dippel's oil' (*oleum animale Dippelii*) (*q.v.*), which when submitted to further distillation yields about 23 p.c. of a hard, firm pitch.

Hard and soft varieties are produced and present the following characteristics: jet black and shining; brittle, and breaking in masses, although distinctly conchoidal; sp.gr. ranges from 1·125 to 1·130. The harder pitches 'twist' at a temperature of 70°, and melt at 98°–100°.

A good sample will yield 63 p.c. of volatile organic matter and 37 p.c. of hard, compact coke, containing from 0·4 to 0·7 p.c. of mineral matter or ash. During the operation of heating and igniting, the characteristic and unmistakable odour of bone or animal oil becomes very powerful and readily distinguishes it from all other pitches. As a solvent, benzene attacks it very imperfectly, but the pyridine bases dissolve it entirely or with the exception of a small quantity of carbonaceous matter. Petroleum spirit dissolves about 30 p.c. Solutions of this pitch in the pyridine bases exhibit no bloom or fluorescence, and when examined spectroscopically merely a cutting out of the violet portion of the spectrum, no absorption bands being visible. Sulphur is present to the extent of 0·30 p.c.

It exhales a somewhat unpleasant odour, very noticeable when warmed. Its chief uses are for tarpaulin and other varnishes.

Stockholm pitch (*wood-tar pitch*). Wood-tar, when submitted to distillation, yields distillates of light oils varying in sp.gr. from 0·840 to 0·880 and about 70 p.c. of pitch. In appearance it is jet black and brilliant, but it is inferior to bone pitch. Its fracture is conchoidal, but it is extremely brittle, crumbling between the fingers. It is slightly adhesive and becomes sticky on gently warming. It has a sp.gr. of about 1·105; at 40° it twists easily and at 82° it melts. When heated and ignited it yields 88–88·5 p.c. of volatile matter, leaving a soft, friable coke ranging from 12–11·5 p.c. and containing from 0·7–0·84 p.c. mineral matter or ash. During the burning off, vapours and odours are evolved impossible to mistake for those of any other pitch, or for other than that of wood tar. Benzene dissolves this pitch completely and the pyridine bases equally well; but petroleum spirit only takes up from 91 to 92 p.c., leaving a small portion insoluble. Sulphur is present but in minute quantity only, not exceeding 0·01 p.c.

A solution of Stockholm pitch shows no bloom or fluorescence, and when examined spectroscopically a cutting out of the violet portion of the spectrum only. No bands are visible nor any indication of chrysene, said to exist in this particular tar or pitch.

Stockholm pitch dissolves almost completely in alcohol and potash lye. When its alkaline solution is boiled a coloured oil passes over possessing a stupefying smell, and when acidified and boiled yields volatile fatty acids. A black mass is deposited as the operation proceeds; on boiling this mass with water, creosote is given off. If the acid and alkaline treatment is repeated several times, the mass is converted into a black powder which, after long boiling with hydrochloric acid, yields to alcohol only a small quantity of resin. The black residue insoluble in alcohol and potash consists of—

	p.c.
Carbon	65·04
Hydrogen	4·89
Oxygen	30·07
	100·00

As wood-tar is a complex mixture of phenoloid bodies, amongst which guaiacol and creosol predominate, and the less volatile fractions contain methyl ethers of pyrogallol and its homologues, it is highly probable that the residual pitch resulting from its distillation at a comparatively low temperature contains amongst its other constituents the methyl ethers of trihydric phenols (*v.* CREOSOTE).

Wood-tar pitch is assumed to possess much of the antiseptic and preservative power of the tar from which it is derived. It finds a considerable outlet for marine purposes and the coating and painting of ships.

Rosin pitch. Rosin or colophony, is the residue left on distilling off the volatile oils from crude turpentine, and when submitted to further distillation, yields definite products, but varying considerably with the temperature and conditions of distillation. In a vacuum or current of superheated steam it may be distilled almost unaltered, but when subjected to dry distillation, as in the ordinary method pursued by rosin distillers, it yields a number of products, consisting chiefly of rosin oil, which passes over to the extent of about 85 p.c., including rosin spirit, water, a powerfully anæsthetic gas containing carbon monoxide, ethylene, butylene, pentene, with a residue of pitch amounting to 1½ cwts. from a ton of rosin.

Rosin pitch is a yellowish-brown substance, hard and compact but easily crumbling on slight pressure. It has a sticky feel, and when warmed exhibits the characteristic odour of resin. Its sp.gr. varies from 1·090 to 1·095;

at a temperature of 35° it twists readily, and at 68° melts. When heated and ignited it yields 82·5 p.c. of volatile matter, leaving a spongy soft coke amounting to 17·5 p.c., which contains 0·58 to 0·7 p.c. of mineral matter or ash. During the heating a strong odour of rosin is given off, readily distinguishing it from Stockholm or wood-tar pitch. In benzene and the pyridine bases it is completely soluble, but petroleum spirit only takes up 86·94 p.c., leaving 13·06 p.c. insoluble: sulphur is present to the extent of 0·26–0·3 p.c.

Solutions of rosin pitch exhibit a deep greenish bloom or fluorescence, but differing from that of coal-tar pitch, which is invariably yellow. Spectroscopically, they merely show a cutting out of the blue and violet portions of the spectrum; absorption bands are absent.

Rosin pitch finds no special use by itself, but is occasionally mixed with other pitches of an inferior description.

Pitches derived from the distillation of petroleum and allied substances. Of these products, ozokerite pitch occupies the most important position. It is obtained from the distillation of crude ozokerite, and the following figures have been furnished by E. J. Mills as representative of the operation:—

Very light oils	20
Heavy oils	50
Paraffin	8
Hard pitch	8
Loss	14
	100

B. Redwood (J. Soc. Arts, 34, 886) gives the products of Galician ozokerite as 5 p.c. of gaseous hydrocarbons, 3 p.c. of naphtha, 6 p.c. of semi-solid 'ozokerine,' 12 p.c. of soft paraffin (melting at 44°–46°), distilled ozokerite (melting at 61°), and black waxy residue. It is a hard, waxy substance breaking with a rough granular surface, and irregular fracture. Its colour is dark amber, inclining to brown; its sp.gr. is 0·950. At a temperature of 50°, it twists and at 85° melts; heated and ignited it yields 9·7 p.c. of volatile organic matter, leaving 3 p.c. of soft, friable coke containing traces only of mineral matter or ash. During this operation the odour evolved is simply that of highly-heated paraffin. It is completely soluble in benzene but not wholly so in the pyridine bases, the solution showing no bloom or fluorescence. Examined spectroscopically, no absorption bands are visible, but a cutting out of the blue and violet portions of the spectrum only, as is the case of the pitches already described.

Ozokerite and ozokerite pitch have been found to possess remarkable electrical qualities, and in admixture with various substances, caoutchouc among them, have formed the subject matter of several patents. Such compounds have found extensive uses for coating telegraph wires and for insulating purposes generally.

Petroleum pitch. In the first distillation of crude petroleum oil, the charges may be run down to a coking point or they may be discontinued at a stage at which pitch or artificial asphaltum would result on cooling.

In appearance it greatly resembles natural bitumen or asphaltum; it is jet black and shining, and breaks with a similar conchoidal fracture. It has a sp.gr. of about 1·120. At a temperature of 45° it 'twists,' at 84°–85°, melts; heated and finally ignited it yields about half its weight of volatile organic matter. The odour evolved is characteristic of petroleum, but differs entirely from that of natural asphaltums, with which it cannot be confounded. Mineral matter is present in minute traces only. Benzene dissolves this pitch completely, affording a solution exhibiting a strong yellow bloom or fluorescence not unlike that observed with coal-tar pitch. It is, however, almost insoluble in the pyridine bases; petroleum spirit dissolves 36·16 p.c. only. The residues from American petroleum contain notable quantities of closed chain hydrocarbons, among which anthracene, phenanthrene, chrysene, chrysogen, and pyrene have been recognised, as also a hydrocarbon called thallene. From Californian petroleum the hydrocarbon picene $C_{22}H_{14}$ has been isolated. When treated with sulphuric acid, it yields a sulphonic acid dissolving in water with a splendid blue green fluorescence. Petroleum pitch, although differing in its physical aspect, may, in many respects, be looked upon as resembling coal-tar pitch.

B. Poro (Gazz. chim. ital. 13, 77) gives the following figures as showing the results of distilling Italian petroleum:—

	I.	II.
Oil	63·5	66·9
Pitch . . .	32·2	28·3

Petroleum pitch has been used in compounding cements, asphalts, varnishes, and patent fuels.

Shale oil pitch is now quite unknown, manufacturers of shale oil preferring to continue its distillation to the extent of coking.

Bibliography.—Lunge's Coal Tar and Ammonia (4th edit.), 1909; Allen, Commercial Organic Analysis (2nd edit.), 1886; E. J. Mills, Destructive Distillation; S. F. Peckham (Amer. J. Sci. [iii.] 28, 105–117); Stripplemann and Engler (Dingl. poly. J. 250, 216, 227, 271, 316, 321); Boussingault (Compt. rend. 96, 1452, 1456); B. Delachanal (*ibid.* 97, 491, 494); S. Bernus (Bull. Soc. chim. de Belgique, 1911, 7).

PITCHBLENDE, or **Uraninite** (Ger. *Uranpecherz*). A uranium mineral which is much sought for as an ore of radium. Its occurrence in the ancient silver mines at Joachimsthal in Bohemia was known as early as 1727; and it was in this mineral that M. H. Klaproth discovered in 1789 the element uranium. The old German names Pecherz, Pechblende, &c., were suggested to the miners by a superficial resemblance of the mineral to pitch and to zinc-blende. The name Uranin, proposed by W. Haidinger in 1845 and later modified by Dana into Uraninite, is sometimes used in a rather wider sense to include the massive variety (pitchblende) and the crystallised varieties ('uranoniobite,' cleveite, bröggerite, and nivenite).

The mineral, although possessing certain points of considerable interest and a high value, is unattractive in appearance. It is opaque and black with a dull pitchy lustre (crystals are brighter and with a sub-metallic lustre) and breaks with a sub-conchoidal to uneven fracture. The streak, or colour of the powder, is brownish- or greenish-black. The only feature that attracts attention is the remarkably high density (sp.gr. 6·4–9·7). This feature serves to distinguish the mineral from the more commonly occurring chromite; in its non-magnetic character it differs from magnetite; and in the absence of cleavage from wolframite—these being minerals often mistaken by prospectors for pitchblende. From some other heavy black minerals, such as columbite and tantalite, the distinction is less easy in the absence of chemical tests. Pitchblende can, however, always be quickly and readily recognised by means of its radio-active character; and without the aid of such simple and portable instruments as the spinthariscope (or scintilloscope) and gold-leaf electroscope the chances of the prospector are small. Although actively sought for since the discovery of radium in 1898, it is a remarkable fact that no new deposits of pitchblende of any importance have been brought to light.

Two distinct varieties, with very different modes of occurrence, are known. One is met with in a massive form, sometimes showing a mamillated or botryoidal surface, in mineral veins together with ores of silver, lead, copper or tin, and frequently associated with ores of nickel, cobalt, and bismuth. The other variety is found as small (1–3 cm. across) octahedral or cubo-octahedral crystals in pegmatite-veins traversing granitic rocks. These two varieties differ somewhat in chemical composition and in sp.gr. (6·4–8 for the massive, and 7·5–9·7 for the crystallised variety).

The mineral has been variously regarded as an oxide of uranium or as a uranate of uranyl, lead, thorium, &c. In composition it is subject to wide variations. The principal constituents are uranous and uranic oxides, but these are present in varying relative proportions. Lead is also invariably present, but it is only the crystallised varieties that contain in addition thorium and metals of the cerium and yttrium groups. Some of the many constituents shown in the analysis are no doubt present as mechanically admixed impurities, this applying more particularly to the massive variety of lower specific gravity. Thus an analysis by F. Janda (Oesterr. Zeitsch. Berg- u. Huttenw., 1902, l. 283; abstr. Chem. Zentr. 1902, ii. 150) of an average sample of the Joachimsthal ore gave: U_3O_8, 49·95; As_2S_3, 0·71; PbS, 1·85; PbO, 0·25; Cu_2S, 1·12; Bi_2S_3, 0·31; Ag_2S, 0·04; FeS_2, 7·93; Fe_2O_3, 1·14; $FeCO_3$, 6·96; Al_2O_3, 3·25; ZnO, 1·09; MnO_2, 0·11; $CaCO_3$, 3·69; $CaSO_4$, 0·89; $MgCO_3$, 0·76; $MgSO_4$, 0·07; SiO_2, 18·55; V_2O_5, 0·02; H_2O, Na_2O, K_2O, P_2O_5, 1·34; $PbSO_4$, $CuSO_4$, Ni, Mo, W, Ra, traces.

Several (22) detailed analyses have been made by W. F. Hillebrand, but he failed to arrive at a definite formula for the mineral (Amer. J. Sci. 1890, 40, 380; Bull. U.S. Geol. Survey, 1891, No. 78; 1892, No. 90; 1910, No. 419). The following analyses, I–V, are by Hillebrand. I, bright crystals from Branchville, Connecticut. II, massive from Johanngeorgenstadt, Saxony; III, massive from Gilpin Co., Colorado; IV, crystals ('bröggerite') from Anneröd, Norway; V, crystals ('cleveite') from Arendal, Norway; VI, (W. Marckwald, Centr. Min. 1906, 761), crystals from Lukwengule, Uluguru mountains, German East Africa.

	I.	II.[1]	III.[2]	IV.	V.	VI.
UO_2	72·25	59·30	58·51	46·13	24·18	87·8
UO_3	13·27	22·33	25·26	30·63	41·71	
ZrO_2	7·20	nil	7·59	0·06	3·66	—
ThO_2		nil	—	6·00		—
CeO_2	—	nil	0·22	0·18		—
$(La,Di)_2O_3$	—	nil	—	0·27		—
$(Y,Er)_2O_3$	—	nil	—	1·11	9·76	—
PbO	4·35	6·39	0·70	9·04	10·54	7·5
FeO	—	—	0·32	—	—	1·0
Fe_2O_3	0·11	0·21	—	0·25	0·03	—
MnO	0·10	0·09	0·16	—	—	—
CaO	0·18	1·00	0·84	0·37	1·06	2·1
MgO	—	0·17	tr.?	tr.	0·10	—
Alkalis	—	0·31	tr.?	tr.	0·23	—
H_2O	0·68	3·17	1·96	0·74	1·23	0·5
He, &c.	n.d.	tr.	0·02	0·17	n.d.	—
SiO_2	0·03	0·50	2·79	0·22	0·90	0·3
P_2O_5	—	0·06	0·22	0·02	—	—
Insol.	0·04	—	—	4·42	1·10	0·2
	98·21	97·93	99·82	99·61	94·50	99·4
Sp.gr.	9·733	6·89	8·068	8·893	7·50	8·84

In the least altered specimens uranium dioxide (UO_2) predominates, whilst in those showing signs of alteration there is more uranic oxide (UO_3) and water. The latter pass into the alteration-product known as gummite, which contains only uranic oxide together with much water. Since the dioxides of uranium, thorium, and cerium have been obtained artificially as cubic crystals, it seems probable that uraninite may be regarded as an isomorphous mixture of these oxides, the formula then being

$$(U, Th, Ce, Pb)O_2.$$

This view is supported by the discovery of the closely allied cubic mineral thorianite (*q.v.*), in which thorium oxide predominates over uranium oxide.

Containing a higher percentage of uranium than any other mineral, pitchblende is correspondingly richer in radium, but this amounts to only one part in five million (*i.e.* about 200 mg. per ton). About 0·1 gram of radium chloride can be extracted from a ton of ore containing 50 p.c. U_3O_8. On the process of extraction employed at the Joachimsthal works, *see* L. Haitinger and K. Ulrich, Sitz.-ber. Akad. Wiss. Wien, 1908, 117, [iiA] 619. The inert gas liberated from pitchblende when the mineral is dissolved in acid or when heated *in vacuô* was first detected by W. F. Hillebrand in 1890, and believed by him to be nitrogen. This led Sir W. Ramsay in 1895 to the discovery in this mineral of terrestrial helium. Argon is also present.

By its alteration in nature pitchblende gives rise to a number of secondary uranium minerals. These are yellow in colour, and are often to be seen as an earthy coating on the surface of hand-specimens of pitchblende: when met with in the upper oxidised zones of mineral-veins, they form a valuable indication of the presence of the mineral. By simple oxidation and hydration it passes into gummite—a heavy, reddish-yellow mineral with a gummy appearance. In the presence of sulphuric and carbonic acids (the former produced by the weathering of iron-pyrites commonly associated with pitchblende), it alters to a number of hydrated and basic uranium sulphates and carbonates—the so-called uranium-ochres (johannite, liebigite, &c.). In the presence of phosphatic solutions it gives the so-called uranium-micas (autunite, *q.v.*, torbenite, &c.).

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[1] Anal. II. includes also: Al_2O_3 ?, 0·20; Bi_2O_3, 0·75; CuO, 0·17; As_2O_5, 2·34; V_2O_5, MoO_3, WO_3, 0·75; SO_3, 0·19.

[2] Anal. III. includes also: As_2O_5, 0·43; $CuFeS_2$, 0·12; FeS_2, 0·24; ZnO, 0·44; TiO_2, trace.

The localities at which pitchblende has been found are relatively few in number, and it is only in three districts that the mineral has been found in quantities sufficient for mining. These are in the mineral-veins of Cornwall, of the Erzgebirge on the borders of Saxony and Bohemia, and in Gilpin Co., Colorado.

In Cornwall, the workable deposits are those of the South Terras mine in the parish of St. Stephen-in-Brannel near Grampound Road, and the Trenwith mine at St. Ives. The occurrence of pitchblende has, however, been recorded in some 25 other Cornish mines in the parishes of St. Just-in-Penwith, St. Ives, Penzance, Gwinear, Camborne, Illogan, Redruth, Gwennap, Wendron, St. Gluvias, Perranarworthal, St. Stephen-in-Brannel, and Lanivet. On the Saxon side of the Erzgebirge it has been found at Johanngeorgenstadt, Schneeberg, Annaberg, Marienberg, Freiberg, Breitenbrunn, Schwarzenberg, and Gottesberg; and on the Bohemian side at Joachimsthal and Schlaggenwald. (On the mode of occurrence at Joachimsthal, *see* J. Stěp and F. Becke, Sitz.-ber. Akad. Wiss. Wien, 1904, 113, [i.] 585.) Other European occurrences are in the mineral-veins of Przibram in central Bohemia, and Rezbanya in Hungary. A specimen has also been described from near Adrianople in Turkey (J. L. Smith, 1848). Near Central City in Gilpin Co., Colorado, pitchblende is worked on the Wood and Kirk lodes. A specimen of doubtful origin has been described from New South Wales (T. H. Laby, 1909). The localities above mentioned all refer to the occurrence of massive pitchblende in mineral-veins.

The crystallised varieties occur as small crystals sparsely scattered in pegmatite-veins, and are occasionally met with as isolated specimens in the felspar quarries in the south of Norway, at several places in the neighbourhood of Moss (Karlshus, Raade, Ånneröd, Elvestad, Huggenäskilen, Skraatorp), near Arendal (Garta quarry and Tvedestrand), and in Sætersdalen (Evje). In the United States, crystals have been found in the felspar quarries at Middletown, Glastonbury, and Branchville in Connecticut. In the Flat Rock mine and other mica mines in Mitchell Co., and Yancey Co., in North Carolina. At Marietta in South Carolina; Barringer Hill in Llano Co., Texas; and rather abundantly in the Bald mountain district in the Black Hills of South Dakota. A Canadian occurrence is in mica mines at Villeneuve, Ottawa Co., Quebec. Finally, crystals have recently been found in a mica mine at Lukwengule in the Uluguru mountains, German East Africa.

Curiously, this ore, now of such great value, was a source of embarrassment to the earlier miners, and it was thrown aside as worthless. Some of the old waste heaps are now being worked over for pitchblende. Since about 1830, it has been used for the extraction of uranium oxides, and in 1853 works were established by the Austrian Government for this purpose at Joachimsthal in Bohemia. The oxides were used in producing rich velvet-black, yellow, and orange colours in porcelain and enamels, and in the manufacture of the well-known fluorescent uranium glass. Limited amounts of the ore have also been used for the preparation of uranium salts employed as chemical reagents and in photography. A more recent application of uranium is in the manufacture of steel for guns.

The limited and uncertain nature of the deposits is well illustrated by the variations in the output of the pitchblende ore. In 1890, Cornwall and Bohemia produced 22 and 25 tons, and in 1897, 30 and 44 tons respectively. After the discovery of radium, the output increased to a maximum of 103 tons in 1905 in Cornwall, and of 52 tons in 1900 in Bohemia. Since then it has decreased to 6 and 8 tons respectively in 1909. Saxony produced only ⅓ ton in 1909. In Colorado, the output of pitchblende has varied between 4 and 20 tons per annum.

L. J. S.

PITTACAL *v.* Wood, Distillation of.

PITTOSPORUM UNDULATUM (*Vent.*). The fruit of this tree which is indigenous to South-Eastern Australia where it is known as 'mock-orange,' yields by distillation an oil of an orange-like odour and contains a large proportion of *limonene* besides small amounts of *pinene* and various esters and an optically inactive *sesquiterpene* (Power and Tutin, Chem. Soc. Trans. 1906, 89, 1083).

PITURI. The leaves of *Duboisia Hopwoodii* (F. v. Müll.), used as a narcotic (Brestowski, Handwörterbuch Pharm. 370). On distillation with steam was stated to yield an alkaloid, a colourless oil, b.p. 243°, called *piturin.* Rothera has shown, however, that the only alkaloid present is nicotine, which forms 2·67 p.c. of the leaves after drying at 60° (Biochem. J. 1910, 5, 193).

PIURI *v.* Indian yellow.

PLAGIOCLASE *v.* Felspar.

PLANT-SPRAYS. Spraying may be taken in a wide sense to embrace the application of solids, liquids, or gases to plants with the object of freeing them from insect or fungoid parasites, or of cleansing them from dead bark, and such adventitious deposit or growth as interferes with the healthy functions of the plant.

Solids.

Many liquid spray-fluids, or washes, contain solids in suspension, but it is only in a few cases that solids are used in the dry state; in such cases they are blown on to the plants by means of bellows, and the operation must be performed while the plants are wet with dew or mist, so that the solid may adhere to them. *Sulphur*, in the form of flowers of sulphur, is applied extensively in this way to hops for destroying mildew and red spider, and in certain other cases it is applied mixed with *lime.* The nature of its action is at present obscure, but most probably depends on its being slightly volatile, for, when used in hot-houses, the most satisfactory results are obtained when it is painted on to the hot water pipes, or otherwise heated. At the same time its effectiveness is increased by the presence of moisture, though it hardly seems possible that the traces of sulphuric acid formed under such conditions can account for its action. Hellebore, consisting of the root-stock and roots of *Veratrum album* (Linn.) and *V. viride* (Ait.) is effective in destroying caterpillars on gooseberries, &c.: it acts chiefly by poisoning their food, but is probably also injurious to them by contact with their bodies. As it is less poisonous than arsenical compounds and loses its properties rapidly on exposure to air, it may be used with safety within a short time of the ripening of the fruit. Pyrethrum, obtained from the ground heads and stems of *Chrysanthemum* [*Pyrethrum*] *roseum* (Web. et Mohr) and *C. Marschallii* (Aschers.), and *C.* (*Pyrethrum*) *cinerariæfolium* [(Trav.) Bocc.], contains an oil which appears to act on insects only by contact. Besides being used in the dry form, it is used as a decoction and also as a fumigant.

LIQUIDS.

A. Insecticides. For a determination of the nature of the insecticide which is likely to be effective in any particular case, a knowledge of the life history of the insect is necessary to indicate at what period it is most vulnerable and by what means it may best be combated. Insects which chew the leaves are best dealt with by poisoning their food, whilst others which pierce the leaves and bark, extracting the juices from below the surface, are best attacked by the application of some corrosive substance to their bodies. The most effective procedure, where practicable, is to destroy the eggs of the insect: for this a corrosive substance is required, and such can only be applied to the plants while these are in the dormant condition. For facilitating insect eggs being reached by a fluid, as well as for reducing the number of crevices in which insects can deposit their eggs, the application of a detergent wash in the winter, to remove dead bark, moss, lichen, &c., from the trees is an important adjunct to an insecticide.

Many of the most popular insecticides and fungicides have come into use by accident, and although practical experiments have introduced considerable improvements in them, much uncertainty still prevails as to the method of their action; and it is remarkable that in very few cases has science provided satisfactory substitutes for these chance selections.

The chief classes of insecticides are (1) vegetable poisons consisting of alkaloids, (2) soft soap, with or without excess of alkali, (3) sulphur and sulphides, (4) phenol, (5) paraffin oil, (6) arsenical compounds, (7) lime.

(1) Of the vegetable poisons, *hellebore* and *pyrethrum* have already been mentioned, and these may be sprayed on to the trees in the form of a 3 or 4 p.c. admixture with water or dilute paraffin oil emulsion. If a decoction is used it should not be boiled. *Quassia* with soft soap is much used for destroying aphis. The wash is made by boiling ½ to 3 lbs. of chips of the wood with 10 gallons of water, and adding ½ to 3 lbs. of soft soap.

Nicotine appears to be by far the most effective of the vegetable insecticides. A decoction of 'denatured' tobacco—which contains about 70 p.c. of tobacco mixed with sulphur, asafœtida and flour—may be used, but owing to the great variation in the nicotine-contents of tobacco, it is better to use nicotine itself. A solution of 0·075 p.c. is very effective for aphis, apple psylla, &c.: it is well to add to the solution 0·5 p.c. of soft soap.

It is noticeable that various alkaloids, such as aconite, hyoscyamine, nux vomica, &c., which are highly poisonous to vertebrate animals, have but little action on insects.

(2) *Soap* is generally used in connection with other substances as in the instances just mentioned, but it is also used effectively alone for killing certain aphides such as those attacking roses. It is probable that its action in such cases is due to its clogging the breathing apparatus of the insect: its low surface tension also enables it to wet bodies more effectively than other spray-fluids, though it may be remarked, a similar action in the case of saponin does not appear to increase the effectiveness of substances to which it is added. Soap is also largely used as an agent for emulsifying paraffin oil. In connection with this, and especially if alkali is added as well, it is used for the destruction of insect eggs, although its chief function under such circumstances is that of a detergent.

(3) *Sulphur* is generally used in the solid condition, as mentioned above, although it occasionally is made into a liquid wash with water and other substances. As an insecticide and still more as a fungicide, the *sulphides* play an important part. The origin of their use seems to have been the application to trees of a liquid used as a sheep dip, and known as the lime-sulphur-salt wash (California wash) or the lime-sulphur-soda-salt wash (Oregon wash). There are many recipes for making these, the more usual being to boil together for 45 minutes 3 to 6 lbs. of quicklime with 3 lbs. of sulphur, 3 lbs. of salt, and a limited quantity of water, the resulting liquid being afterwards diluted to 10 gallons. In the Oregon wash, about 1 lb. of caustic soda is added in addition to the above materials, and the heat generated on adding water to the mixture is sufficient to obviate the application of external heat. A wash of this strength can be used only on dormant trees, and is then more effective when applied hot; but at a lesser strength it is now being used on trees in leaf, chiefly as a fungicide. The wash always contains a considerable proportion of unaltered lime, the sulphur going into solution as calcium thiosulphate and pentasulphide. The latter undergoes rapid change, even in absence of air, the pentasulphide becoming converted into thiosulphate with the liberation of sulphur, and the thiosulphate into sulphite and more free sulphur: the sulphite ultimately oxidises to sulphate. Where caustic soda is used in its preparation, the sulphur reacts with it in preference to the lime. The method of operation of this wash is uncertain. It is used

habitually in the Western States of America for combatting San José scale, and according to certain experiments, none of the substances which it contains, when used separately, have any effect on the scale: according to other authorities, a mixture of potassium sulphide and lime is as effective as the wash. It appears that its action is in part mechanical, the sulphur deposited from it on to the trees glueing the scales to the bark and preventing the egress of the young insects. What function the salt performs is obscure, and according to some investigators it may be omitted without detriment. Owing to the excess of lime present in it and to the destructive action of sulphides on lichen, &c., the wash is a good detergent.

Lime and sulphur mixed with water without heating are sometimes used for aphis, mites, and red spider, being preferable to sulphur by itself; such a mixture always contains some products of the reaction of the two substances. Calcium sulphide solution is also used for the same purpose, but potassium sulphide is preferable, as soft soap can be added to it without causing decomposition: 3 to 10 ozs. in 10 gallons are the proportions recommended. It can also be mixed with an emulsion of paraffin oil.

(4) *Phenol*, either dissolved by itself in water, or with the addition of soap or glycerol, has been tried as a general insecticide without much success, but a solution of carbolic acid soap is very effective for certain aphides as well as mildews (*e.g.* of roses), and phenol figures as one of the ingredients of several proprietary insecticides which are now in use.

(5) *Paraffin oil* was used for spraying purposes very soon after it was first obtained. The undiluted oil cannot be used on trees, even in the dormant season, without some risk of injury, but injury does not always follow, even when the trees are in leaf, and it is a very satisfactory remedy to apply in cases (*e.g.* woolly aphis) where the eradication of a pest from a plantation is of more importance than the possible injury to some of the trees. In that case, a pneumatic sprayer should be used, which distributes the liquid in the form of a very fine mist. A good quality lighting oil must be used, higher boiling oils are certain to injure the trees, and so do the more volatile oils (petrol), due, probably, in the latter case to the cold produced by evaporation. Mixtures of oil and water, unless quite dilute, appear to do more damage than undiluted oils. The admixture of oil with water used to be effected by pumping the liquids from separate containers into one delivery hose fitted with a spraying nozzle. It is now more general to emulsify the oil in the water either by means of soft soap or of certain finely divided solids, such as the basic sulphates of iron or copper, obtained by precipitating the normal sulphates with lime-water or milk of lime. For plants in leaf, the proportion of oil should not exceed 1½ p.c., but where they are dormant 6 or 7 p.c. may safely be used. Much larger proportions are often used in America. For dormant trees it is usual to add to the emulsion 2¼ p.c. of caustic soda, which makes the wash a powerful detergent, as well as an insecticide as regards the eggs of certain insects. In that case, a basic sulphate should be used instead of soap as an emulsifying agent, although there are special brands of soap which act fairly well under the circumstances; those containing a large proportion of stearin yield a sufficient supply of small insoluble particles to prevent total de-emulsification when the potash soap is flocculated by adding the soda. Emulsions of paraffin may be used in conjunction with most insecticides and fungicides.

(6) *Arsenical compounds.* These supply some of the most powerful insecticides for leaf-eating insects. An aceto-arsenite of copper (Paris green), made by the action of arsenious oxide on verdigris, was one of the first of these substances to come into use, but it is liable to injure the foliage, the leaves becoming scorched, and often falling. This action is intensified if the Paris green contains excess of arsenious oxide, as it often does, and it is well to guard against this by the addition to it of an equal weight of lime. Calcium arsenite, made by boiling arsenious oxide with lime, is also used, although more frequently in the form of London purple, which is a waste product from dye-works and contains 75 p.c. of the arsenite. The compound which has come most into favour of recent years, chiefly on account of its causing very little leaf-scorching, is lead arsenate, also called gypsine, from its being first used for the gipsy moth caterpillar. When prepared by the precipitation of lead acetate by sodium arsenate (7 oz. of the acetate to 3½ oz. of the crystallised, or to 2 oz. of the 'dry' arsenate for every 10 gallons) it consists of the triplumbic salt, $Pb_3(AsO_4)_2$, but when lead nitrate is used, the product consists chiefly of $Pb_2H_2(AsO_4)_2$. Both substances are slightly soluble, the latter being the more soluble of the two, and they are in a fine state of division which facilitates their distribution over, and adherence to, the leaves. The insecticide is sold in the form of a paste, mixed sometimes with other materials, and is preferable to the home-made material, inasmuch as it is free from the small proportion of acetic acid liberated in the reaction, which tends to cause leaf-scorching.

(7) *Lime* has been used of late years together with salt, as an insecticide in special cases (apple psylla). The lime-salt wash is made by slaking 15–20 lbs. of lime, adding 2–3 lbs. of salt, ½–1 lb. of water-glass, and making up to 10 gallons. It is applied to the trees, as hot as possible, a few weeks before the buds open. The wash appears to act partially by destroying the eggs and partially by glueing them up and preventing the egress of the insects. What function the salt performs it is difficult to see. Strong brine will destroy insect eggs by depleting them of their liquid contents, but the salt is hardly present in this wash in sufficient proportion for such an action.

B. **Fungicides.** Sulphur, and the sulphides previously described, are important fungicides, the latter being of special use in the case of surface moulds or mildews. Phenol and the salts of iron appear to have but very feeble fungicidal properties, and mercuric chloride, although of great value in the laboratory, has not been successfully applied to plants. By far the most important fungicide appears at present to be copper, and it has been applied in a great variety of forms.

The problems of fungicidal action are complex and, at present, very obscure. A fungus destroys its host-plant by the development of mycelium, or thread-like roots, which penetrate and break up the plant cells. As these do their work within the body of the plant, they cannot be reached by any fungicide. Remedial measures must depend on killing the spores or seeds of the fungus, or else on protecting the plant in such a way that fungus spores alighting on it will find conditions unsuitable for germination. A fungus being, like its host, a plant, anything deleterious to it is likely to be deleterious to the host-plant also, and a scorching action on foliage has been found to be a general concomittant of fungicidal action, although under certain weather conditions such damage does not take place. When a plant is in the dormant condition and a strong fungicide can be used on it, the fungus also exists in the form of resting spores which are very resistive to treatment.

For a substance to be operative it must either be soluble to start with or become soluble during use. The insoluble copper compounds used as fungicides apparently become soluble by the agency of carbon dioxide, copper sulphate being the substance liberated; and the evidence at present seems to be against the view that anything excreted by the fungus itself or by the host-plant acts as a solvent agent. Fungus spores, while actually germinating, or the mycelium while in a state of activity, would doubtless excrete substances capable of dissolving copper compounds, and the leaves of some trees (*e.g.* the lime), certainly do so, as do the leaves of many other trees when bruised; but no such action has yet been established, either with dormant fungus spores or with the sound leaves of fruit trees. The protective action of a fungicide consists in its forming a coating on the leaf, generally of copper carbonate, which is slightly soluble and which, therefore, prevents fungus spores from germinating there. But protection may also occur through the imbibition of soluble copper into the substance of the leaf itself, for it has been shown that copper is thus absorbed, becoming apparently substituted for the iron which is normally present therein. It appears that both the fungicidal and the scorching action of soluble copper compounds is dependent solely on the amount of copper contained in them, unless the acid radicle present has a fungicidal action of its own, and the intensity of the effect is approximately a logarithmic function of the strength, so that often very little is gained by a considerable increase in strength.

The use of copper compounds originated in verdigris having been applied to roadside vines to prevent depradations, with the result that such vines were found to remain free from mildew. This led to the use of copper sulphate, to which lime was next added to neutralise the acid which was supposed to be responsible for the scorching produced. Such a mixture was known as Bordeaux mixture, and it is still the most extensively used fungicide. The proportions of ingredients recommended have varied largely at different times, but at present it is generally made with 8 lbs. of lime and 8 lbs. of copper sulphate to 10 gallons, and it is obtained in the most satisfactory state of subdivision by adding the sulphate in the form of a strong solution to the lime, previously slaked and mixed with the bulk of the water. The action of lime on copper sulphate results in the formation of a series of basic salts, of which $4CuO,SO_3$ is the lowest, and is that formed when the lime is just sufficient to precipitate the whole of the copper. When the amount of lime is increased until the liquid becomes barely alkaline, the compound formed is $10CuO,SO_3xCaSO_4$, which is a very bulky substance, settling slowly in the liquid, and very suitable, therefore, for spraying. With a still larger proportion of lime, such as is used for Bordeaux mixture, it is the latter body which is formed at first, as the water present is insufficient to allow the whole of the lime to react at once, but this excess of lime gradually dissolves and the precipitate is converted into another compound, $10CuO,SO_3,2CaO$, mixed with copper cuprite, this mixture forming a violet blue compact precipitate, little suited for spraying. Bordeaux mixture should, therefore, be used as soon as possible after preparation. Most of the basic sulphates are insoluble, but are decomposed by carbon dioxide reproducing copper sulphate, but only in amounts representing a small proportion of that used in making them, as is evident from the equations:

$$10CuSO_4+9CaO=10CuO,SO_3+9CaSO_4$$
$$10CuO,SO_3+4{\cdot}5CO_2=CuSO_4+4{\cdot}5CuCO_3,CuO$$

although the proportion liberated in this state is found to be considerably in excess of that here indicated, the additional SO_3 required for the production of the excess being derived from the calcium sulphate, which is not present as such, but as an integral portion of the basic sulphate itself. The copper sulphate liberated acts directly as a fungicide in the manner above indicated, whilst the copper carbonate formed supplies a protective coating to the leaf. With ordinary Bordeaux mixture there is considerable excess of lime present, which decomposes any sulphate as soon as it is formed, the practical result being that only 2 or 3 p.c. of the copper sulphate taken to make it becomes converted again into sulphate, whereas about twenty times that proportion is obtained when pure $10CuO,SO_3$ is used, but the reduction in the proportion of active fungicide in the case of the ordinary mixture is partially counterbalanced by an increase in the protective carbonate formed. With ordinary Bordeaux mixture it is only when the deposit dries up and liquid communication between the particles of lime and basic sulphate is interrupted, that any copper sulphate is formed by the action of carbon dioxide. It seems too that the sulphate cannot remain very long as such on the leaves for it is gradually converted into carbonate by the calcium carbonate present.

It has been shown that carbon dioxide at the low pressure at which it normally exists in the air, does not react with the basic sulphates so as to liberate permanently the amount of copper sulphate indicated in the above equations; but carbon dioxide is evolved in large quantities from foliage, and the reaction actually occurring probably approximates to that indicated. Judging by the fungicidal results, the proportion of soluble copper liberated from the compound $10CuO,SO_3$ is six to twelve times that liberated from ordinary Bordeaux mixture containing the same weight of copper, instead of twenty times as much, as experiments with pure carbon dioxide suggested. This superior efficiency of $10CuO,SO_3$ has led to its introduction on to the market in the form of a paste. The absence of solid particles of lime which clog the spraying nozzles and the avoidance of the labour of home manufacture, are advantages claimed for it; but important advantage probably consists in the reduction of the amount of copper distributed over the land by the spraying. Seedling plants are remarkably sensitive to the toxic action of copper, the effect of one part of the metal in 10,000,000 of water being recognisable on barley seedlings. Copper carbonate is soluble in rain water to a much greater extent than this, and the amount of copper reaching the soil in a single spraying would be sufficient to convert the soil-water in the upper nine inches into a solution containing enough of the metal to render it markedly toxic. So far as casual observations go, no deterioration of soil has been observed as a consequence of Bordeaux spraying, indicating that the ultimate compound formed by the metal must be a body less soluble than the carbonate, but until more is known on the subject it is eminently desirable to diminish the accumulation of copper in the soil as much as possible. Herbage under trees may also become poisoned by copper spraying. Former experiments on this point had indicated that no such danger existed, but an instance has occurred in which a large number of sheep were killed by copper poisoning in a grass orchard which had been sprayed. Fruit should not be sprayed with copper within 5 or 6 weeks of its ripening.

Various dried Bordeaux mixtures are in use as substitutes for the ordinary mixture. They consist mainly of the basic sulphate $4CuO,SO_3$, and generally contain some soluble copper. The amount of soluble sulphate liberated from them by the action of carbon dioxide is much less than that indicated by their composition, the comparatively large particles of which they are composed becoming encased in the carbonate formed, thus preventing the completion of the action. They are comparatively dense powders, which renders them inferior as spraying materials.

Copper carbonate itself is sometimes applied direct to the trees, as a substitute for Bordeaux mixture, and is known as soda Bordeaux. It is made by mixing 1·84 lbs. of crystallised sodium carbonate with 1 lb. of copper sulphate to make 10 or 20 gallons of wash. The precipitated carbonate consists of $5CuO,2CO_2$, some of this (to the extent of 0·003 p.c. of copper) remaining dissolved, while more copper is found in solution, if either a smaller or larger proportion of sodium carbonate is used, a cupricarbonate being formed in the latter case. The precipitated carbonate soon becomes granular and compact, changing into malachite, $2CuO,CO_2$, so that the wash should be used at once after being made. The large amount of copper contained in it is a disadvantage, and the acid sodium carbonate, present as one of the products of the reaction, is liable to injure delicate foliage.

The addition of treacle to Bordeaux mixture has been advocated as a means of rendering some of the copper soluble and also of increasing its adhesive properties. If the mixture is made with pure materials, the copper present dissolves in the dextrose of the treacle, either entirely or partially, according to the proportions, to give a violet solution which begins decomposing almost at once with the liberation of cuprous oxide. Such a mixture may either be very rich in dissolved copper or may consist of nothing but cuprous oxide, and is clearly very unsuitable for a spray fluid.

Numerous other copper compounds have been tried as substitutes for Bordeaux mixture, but without much success. Several of them are cuprammonium compounds which present difficulties in preparation of definite strengths, and there is much risk with them of the ammonia injuring foliage. Copper sulphate itself may be used, up to a strength of 0·25 p.c. copper, on trees while dormant.

C. **Detergent washes.** Lime-washing the trunks and main branches of trees has long been practised as a means of cleansing them and reducing insect attacks. The substitution of caustic soda for the lime produces more satisfactory results, and permits of the whole tree being treated by spraying. A wash containing 2¼ p.c. of caustic soda is recommended, and its efficacy is further increased, both as a detergent, and still more as a direct insecticide, by the addition of about 6 p.c. of paraffin oil, this being emulsified with it by the agency of the basic sulphates of iron or copper. A recipe, the origin of which is unknown, is very widely circulated, in which about half of the above quantity of caustic soda is supplanted by an equal weight of potassium carbonate; but it has been proved that the latter is practically valueless as a detergent, and the use of it merely entails loss of money and efficiency.

GASES.

Hydrocyanic acid is used in the fumigation of hot-houses for the destruction of plant lice, &c.; it is also used in many countries for disinfecting imported nursery stock, and in California it is applied to peach trees in plantations for scale, each tree being covered with a tent during the operation. To avoid danger to the operator, potassium cyanide is wrapped up in paper, and lowered from outside by means of a string into a jar of dilute sulphuric acid. This is not always satisfactory, as the paper sometimes becomes converted into parchment paper and the cyanide becomes coated with potassium sulphate, which arrests the action. A better method is to enclose the cyanide in a little zinc canister made for the purpose and place the whole in the acid. For each 100 cubic feet of space, ⅓ to ¼ oz. of 'lump' potassium cyanide is used, and for each ounce of the cyanide, one liquid ounce of acid previously diluted with 3 to 4 ounces of water. 'Stick' cyanide contains only 40 p.c. of potassium cyanide, and proportionately larger quantities of it must be used, whereas if sodium cyanide is taken (which is preferable on account of its being more easily soluble), the above quantities must be reduced by 25 p.c. Hydrocyanic acid is liable to cause some injury to young plants, and in fumigating these they should not be exposed to the direct stream of gas as it ascends from the generating vessel. Its action in destroying insect eggs is somewhat uncertain, and in the case of green-houses it is often necessary to repeat the fumigation after a fortnight's interval, to destroy insects which have hatched out from the eggs. For freeing nursery stock from woolly aphis, an advantageous substitute for fumigation is to immerse the trees bodily in water at 115°F. for 10 minutes.

Sulphur, as already mentioned, probably acts as an insecticide owing to its volatility, and it is often used for fumigating houses by heating it, taking care not to let it catch fire. Smouldering tobacco and pyrethrum are used in the same way.

S. P. U. P.

PLASMON. Milk casein made soluble by alkalis.

PLASTER OF PARIS *v.* CALCIUM.

PLASTIC CLAY *v.* CLAY.

PLATINOTYPE PROCESS *v.* PHOTOGRAPHY.

PLATINUM. Sym. Pt. At.wt. 195·2. In the group of the platinum metals are included platinum, iridium, rhodium, palladium, ruthenium and osmium. They are almost entirely obtained from the crude 'platinum' which, originally present in traces in the older plutonic rocks, has become concentrated in the alluvial deposits derived from their disintegration.

The crude platinum is found in these alluvials as water-worn, rounded or flattened grains or nuggets or, very rarely, as cubes or octahedra, together with brighter, almost micaceous flakes of the alloy of iridium and osmium known as osmiridium or iridosmine. True nuggets are extremely rare, although one from the Urals, weighing over 250 oz., is exhibited at the Demidoff museum in St. Petersburg, and one weighing about 24 oz. has been found in Colombia. Platin-iridium, an alloy of platinum and iridium, practically free from osmium, is also commonly associated with the ordinary crude platinum, while native palladium occurs with native platinum and in association or alloy with gold in Brazil, the Republic of Colombia, the Harz, &c., and in copper-nickel ores in Ontario, Wyoming, &c.

Chromite, magnetite, ilmenite, and other heavy minerals which occur in serpentines and other alteration products of the parent rocks, are also found together with gold, in association with the crude platinum, but it is curious that, although gold and tin commonly occur together in alluvial deposits and, like the rare minerals tantalite, columbite, molybdenite, monazite, &c., are derived from plutonic rocks similar to those yielding platinum, they do not commonly occur in alluvials which are sufficiently rich to be worked for that metal.

Platinum occurs in minute traces in most river beds the sands of which come from the older rocks, and has been found in dolomite, barytes, wollastonite, and many other rock-forming minerals produced by the metamorphism of such rocks, and in the metalliferous minerals associated with them. The presence of copper and iron in alloy with platinum in most varieties of crude platinum from the most widely separated districts is interesting, and the fact that it has been found in meteoric iron with nickel and in the cupriferous nickel ores of Sudbury in Ontario is deserving of special mention. The actual commercially workable sources of platinum are extremely limited, and there is no reason to anticipate the discovery of any new fields which are likely to add materially to the production except as by-products from smelting operations.

Crude platinum commonly contains sufficient iron to be magnetic, so that it may be separated roughly from osmiridium by a carefully regulated electro-magnetic separator, but the danger which exists, of removing platinum with the magnetic or slightly magnetic iron sands, &c., which would require to be first removed from roughly dressed alluvial by a comparatively weak magnet, is likely to prevent the use of electro-magnetic separators on a commercial scale.

As platinum does not amalgamate with mercury, the removal of native gold from native platinum is a simple matter, but this very fact results in the loss of much of the latter metal in alluvial workings where platinum occurs in small proportion as compared with the gold and is, in too many cases, allowed to pass away with the waste from the amalgamation. It is impossible to estimate the extent of this loss, but it is a fact that increasing proportions of platinum and the allied metals are being recovered in the refining of bullion obtained from alluvial gold, and that all ordinary refined gold contains platinum and iridium. From this source and from the treatment of the matte from the smelting of the nickel-bearing ores of Sudbury—where the mineral sperrylite (platinum arsenide, $PtAs_2$) occurs with nickeliferous pyrrhotine—of the copper ores of Wyoming, and of the ores of lead and silver which commonly contain platinum in traces, a considerable increase in the production of the platinum metals may be hoped for; but there is no reason to expect any material increase over the present alluvial output, and no ore *in situ* rich enough in platinum to justify direct treatment for its recovery, has yet been discovered. The fact that platinum cannot be amalgamated with mercury or profitably extracted by alkaline cyanide, renders it impossible to treat platiniferous ores similarly to gold ores, even if they occurred to the same extent and were of the same richness as the latter. In this connection, it may be stated that the United States Geological Survey Report on the Production of Platinum, &c., for 1910, estimated the production of platinum in the United States from the refining of bullion in 1910, as about 500 oz., a large increase on the recovery from that source in 1909.

Selected platiniferous nickel ore from Sudbury and the copper-nickel matte obtained from the smelting of the ore, have been treated by the Port Orford Copper Company in the United States and by others, for the extraction of platinum and the allied metals, and there is good reason to hope that a substantial increase in their production will be obtained from this and similar sources.

It is impossible to obtain trustworthy statistics as to the total world's production of either crude or refined platinum. The official figure for Russian production of crude platinum in 1910 is 175,716 oz., but it is stated that the actual production was about 275,000 oz. and it has even been given as over 300,000 oz. In other countries, the statistics commonly include much old platinum which has been worked up, while, in some cases, part of the official figures are for real platinum and others for crude, *i.e.* for raw alluvial concentrate yielding anything between 60 p.c. and 80 p.c. of platinum with perhaps 10 p.c. of other metals of the platinum group.

The following figures issued by the United States Geological Survey in November, 1911, include probably the most accurate estimates of the production of the principal producers in 1909 and 1910. The production is given in troy ounces of crude platinum (which may be taken as roughly containing 70 p.c. of platinum), except in the case of the United States matte and bullion, where the figures given naturally refer to refined platinum :—

	1909	1910
Russia	264,000	275,000
Republic of Colombia . .	6,000	10,000
United States, domestic crude	672	390
United States, from foreign and domestic matte and bullion	600	1000
Borneo and Sumatra . .	500	200
New South Wales . .	440	332
Canada	30	30
	272,242	286,952

The following analyses are sufficiently typical to indicate the general character of crude platinum, &c., from various localities. They are somewhat old (the first five being by Deville and Debray) and the ruthenium has been ignored except in the case of the osmiridium, but they are probably as trustworthy as any which have been published :—

——	Pt	Ir	Os	Rh	Pd	Ru	Au	Cu	Fe	Osmiridium	Sand
Crude Platinum											
Choco (Colombia)	86·2	0·85	—	1·40	0·50	—	1·00	0·60	7·80	0·95	0·95
California	85·5	1·05	—	1·00	0·60	—	0·80	1·40	6·75	1·10	2·95
	79·85	4·20	—	0·65	1·95	—	0·55	0·75	4·45	4·95	2·69
Australia .	61·40	1·10	—	1·85	1·80	—	1·20	1·10	4·55	26·00	1·20
Urals . .	76·40	4·30	—	0·30	1·40	—	0·40	4·10	11·70	0·50	1·40
„ (Nischnei-Tagilsk) .	75·10	2·60	2·30	3·50	1·10	—	0·40	1·00	8·10	0·60	—
Borneo . .	70·21	6·13	1·15	0·50	1·41	—	—	0·34	5·80	—	—
Platin-iridium											
Urals . .	19·64	76·85	—	—	0·89	—	—	1·78	—	—	—
Brazil . .	55·44	27·79	—	6·86	—	—	—	3·30	4·14	—	—
Osmiridium											
Urals . .	10·08	55·24	27·23	1·51	trace	5·85	—	trace	trace	—	—
California .	—	53·50	43·40	2·60	—	0·50	—	—	—	—	—
Australia .	—	58·13	33·46	3·04	—	5·22	—	0·15	—	—	—

The purest nugget yet analysed contained 86·5 p.c. of platinum. They usually contain between 70 p.c. and 85 p.c., iron being the principal impurity, although copper is invariably present. In one nugget from the Urals, 19·5 p.c. of iron has been found.

Crude platinum is separated from alluvials by ordinary hand sluicing or dredging operations, and may be regarded as a by-product in gold dredging in the United States, Canada, Colombia, and many other districts, and as the main product in the Urals which, from five districts, is stated to produce about 95 p.c. of the world's output. In the Urals, about 80 p.c. of the total yield is at present obtained by hand sluicing, but dredging is likely to largely supplant hand work in the near future.

The metal occurs in an eroded peridotite covering a large area, but, although increased activity has arisen through the rise in the price, production is almost stationary, and any increase must be dependent upon dredging operations dealing with deposits too poor to permit of treatment except on an enormous scale and under more economical conditions. A large proportion of the total production is smuggled across the frontier, and it is believed that the officially certified output of 176,716 oz. of crude platinum for 1910, should be increased by at least 100,000 oz., to allow for such illicit and other additional production.

It has been stated that the alluvial treated in Russia averages between 30 and 35 grs. of crude platinum per ton, but this probably refers to the material actually washed by hand labour and ignores the overburden which has first to be removed. It is probable that the material actually handled averages under one-third of that amount, or well under one part per million.

Apart from Russia, the most important producer is the republic of Colombia which in 1909 yielded, from two districts on the Pacific side of the state, about 6000 and, in 1910, about 10,000 crude ounces. The output of platinum in Colombia is, however, so small in comparison with the gold, which constitutes the main value of the alluvials, that the industry has not hitherto been regarded of especial importance, although the total production to date is stated to have exceeded half a million ounces of crude platinum and although platinum was obtained from Colombia or, at any rate, from South America, nearly a century before it was discovered in Russia.

In 1819, grains of a white metal were found in the auriferous gravels of the Urals, and in 1823, the metal was proved to be platinum.

From 1825 to 1845, the Russian Government absorbed all the output for their coinage but in that year such coinage was discontinued, and a heavy fall occurred in the price previously commanded by Colombian platinum and, until recently, platinum has only been produced in South America by natives operating with the crudest appliances and only when necessity compelled them to work.

The platinum industry is practically controlled by three firms, Johnson, Matthey and Co., of London; Heraeus and Co., of Hanau; and Quennessen de Belmont, Legendre and Co., of Paris, who purchase and refine practically all the Russian output and a large proportion of the small quantity produced elsewhere. It is true that two firms in St. Petersburg refine between 6000 and 10,000 oz. yearly, and that between 5500 and 6000 oz. is obtained yearly in the United States from home and imported crude ore, matte and bullion, but the whole forms an extremely small proportion of the world's output of nearly 290,000 oz. The other metals of the platinum group are present only in small proportion, and their recovery, notwithstanding their importance and high market value, is entirely dependent on the amount of crude platinum obtained by the miner or concentrated by the smelter, and the skill with which it is worked up by the metallurgist.

It is interesting to note that Messrs. Johnson, Matthey and Co., who introduced autogenous soldering with the oxy-hydrogen blowpipe and who are still the largest refiners of the metal, were the first to engage in the industry as a commercial enterprise and have throughout been the most active in introducing improvements in the metallurgical and chemical treatment of crude platinum, in producing the various platinum metals in a state of purity or as alloys of definite composition and for special uses, and in generally developing both the commercial and scientific sides of the industry. From the point of view of the analyst and physicist, probably no rare metals are of such importance in their work or so difficult to obtain in a condition suitable to their requirements.

At the close of the eighteenth century, Marggraf, Achard, and others prepared a platinum crucible by igniting an alloy of platinum and arsenic, and hammering up the mass of malleable platinum thus left and, for some years from 1787, Jeanety, a working silversmith, employed the method commercially in Paris. The metal was, however, very impure. It failed to withstand high temperatures and was unsatisfactory for the fusion of alkaline carbonates. The precipitation of the double chloride of platinum and ammonia, and the presence in it of the red iridium salt, were known even at that period, and Count Puschkin, Vice-President of the Department of Mines of St. Petersburg, referred to it in 1797 as well known and, at the same time or a year or two later, suggested the use of the precipitate as a means of preparing pure platinum after first converting it into an amalgam with mercury.

Between the years 1800 and 1808, Thomas Cock, a relative of a grandson of the founder of the firm of Johnson, Matthey and Co., elaborated the method of dissolving the crude metal in *aqua regia*, precipitating it as the double chloride of platinum and ammonium, and igniting the washed precipitate to spongy platinum under conditions which render it suitable for being hammered and worked up into crucibles, &c. This process, which was afterwards commonly known as Wollaston's, on account of his having described it, with many improvements, in the Bakerian lecture for 1828, is fully described in many works on Chemistry, and is the basis of all present methods of refining platinum. The platinum thus obtained may contain as much as 2 p.c. of iridium with traces of other of the platinum metals, and is at least as good for ordinary purposes as pure platinum. The insoluble matters left by the *aqua regia* treatment, contain osmiridium, and various impurities, such as chromite, zircon, spinel, &c., originally present in the crude platinum, while the mother-liquor from the double platin-ammonium precipitate contains most of the rhodium, palladium, and ruthenium, together with a small proportion of the iridium and osmium. The insoluble matter and the mother-liquor are both worked up for the separation of these metals, as stated later.

The important and increasing production of the platinum metals through concentration during the 'bessemerisation' and final electrolytic treatment of copper ores and, particularly, of the matte obtained from the nickel-copper ores of Sudbury, Ontario, and from the arsenical cobalt nickel ores, associated with native silver in the Cobalt district of Ontario, has already been mentioned. These and other metallurgical operations in which the precious metals become naturally concentrated in a product requiring final electrolytic purification or acid treatment, are the only ones from which any substantial increase in the output can be expected, but they are sufficiently promising to deserve special attention from both metallurgist and chemist. No trustworthy information is available as to the exact procedure, but it appears to be mainly confined to the treatment of the anode mud obtained during the final electrolytic purification of the metals or the residue left by the acid or other treatment of the matte. The 'mud' or residue contains the gold, silver, and platinum metals together with selenium, bismuth, &c., and is melted down and refined by ordinary chemical processes.

In 1910, over 2100 oz. of palladium, in addition to 1000 oz. of platinum and an unknown amount of iridium, rhodium, and ruthenium, were produced in the United States from the treatment of bullion and matte, the latter of which was largely obtained from the Ontario ores.

Platinum is a tin white metal, harder than copper, capable of taking a high polish and, when pure, ranking next to gold and silver in malleability and ductility. Its sp.gr. is 21·46 (G. Matthey). It melts at 1710°+50° as determined with a resistance pyrometer by Harker, or at about 1753° as determined with the optical pyrometer by Wardner and Burgess. It is stated by Knocke to commence to volatilise *in vacuô* at 540°, while, according to Hulett and Berger, volatilisation commences at 800° in air, but does not occur in the absence of oxygen. The extent of such volatilisation is, however, still doubtful and, under normal conditions, is a matter of only slight technical importance, except in so far as it emphasises the necessity for cleanliness of utensils and special care in the method of heating and in ensuring perfect combustion of the fuel. The loss experienced with pure platinum vessels at the strongest heat to which they are ordinarily subjected, is known to be negligible, although Moissan has volatilised it and the other platinum metals, in the electric furnace.

The expansion of platinum when heated, is less than that of any other single metal, its coefficient of linear expansion being ·00000907 at 50° according to Fizeau, or ·00001130 at 1000° according to Le Chatelier. This expansion being about equal to that of ordinary glass, has resulted in the use of platinum for a large variety of electrical purposes, and there is a constant increase in the gross consumption for the leading-in wires of electric lamps, although improvements in the construction of the lamps themselves have resulted in less platinum being employed per lamp. For the same reason, *i.e.* because its expansion is about equal to that of the material of which the best artificial teeth are made, very large quantities of platinum are used in dentistry, in addition to its employment in alloy with silver. Its high melting-point and great electrical resistance, and the absence of oxidation, render it the best medium for localising the heat and economising the current in electric furnaces for scientific purposes where efficiency and convenience are more important than saving in cost.

Although the most useful of all metals for general scientific purposes, it is attacked by many reagents which would scarcely be expected to have any action upon it, and the greatest care is essential in its use. Practically all other metals will alloy with it, and all—excepting certain of the other platinum metals—lower its melting-point. For this reason, no metal or metallic compound in presence of a reducing agent should be heated in it, nor should cyanides, sulphides, or arsenides, or arsenates or phosphates (in presence of a reducing agent or, practically speaking, under any circumstance) be heated in it. Caustic alkalis or alkali nitrates or the alkaline earths or peroxides or per-salts generally should also not be fused in it, as they attack and partly dissolve the metal as well as tend to render it permanently brittle.

The action of many salts and mixtures of salts on platinum is somewhat obscure. Fused ammonium sulphate or the halogen salts of the alkali metals have little or no action upon it, but a mixture of this sulphate with ammonium or potassium bromide, corrodes it rapidly. The alloys of platinum and iridium are more resistant to ignition and to corrosion, &c., by reagents than pure platinum, but it is stated that platinum vessels containing 3 or 4 p.c. of iridium are more liable than pure platinum to form a covering of soot from illuminating gas and to be more corroded thereby. The necessity for care in ensuring perfect combustion when using water-gas or gas containing carbon-monoxide, is well known, although the cause is not clear. It may possibly be due in some degree to the presence of iron carbonyl as well as to the imperfect combustion of the carbon monoxide.

The power of platinum (referred to later) to occlude gases, has doubtless much to do with the brittleness which the metal acquires if used without due care and without frequent burnishing to overcome the porosity which, at first only superficial, gradually extends to the interior, if not overcome by frequently rubbing down the surface. Acid salts and pure unmixed acids are practically without action upon it, and the demand for platinum for sulphuric acid concentration has accounted in the past for the locking-up of more of the metal than any other use. The first large piece of platinum apparatus for this purpose was made by Messrs. Johnson, Matthey and Co. It was capable of holding 300 lbs. of sulphuric acid and was employed over a hundred years ago by Sandman in the Borough. Since the Paris Exhibition of 1855, when the makers exhibited a gold-lined platinum still, Mr. J. S. Sellon, one of the directors of the firm, has superintended the manufacture of hundreds of stills aggregating nearly 50,000 oz. in some years.

Of late years platinum has been largely replaced in sulphuric acid concentration by gold, and, more recently, by silica-glass or, where the presence of traces of iron is unimportant, by vessels of specially resistant alloys of iron and silicon, such as ‘tant-iron.’ Its use in dental alloys, although always large, becomes substantially reduced when the price rises, so that much of the metal which would otherwise become permanently locked-up, is released for other uses; while the employment of platinum and its alloys for self-lighting lamps—an extremely old use which became again fashionable during the last decade—has apparently been finally given up in favour of spirit lamps ignited by the spark from a pyrophoric alloy containing cerium and acting like flint and steel.

On the other hand, the use of platinum black as a catalysing agent (as referred to later) in the manufacture of sulphuric acid, is increasing rapidly and is causing the locking-up of a further large quantity of the metal; while its use in electro-chemistry and pyrometry and in the sparking plugs of explosion engines, and the collectively large and constantly increasing use of small pieces of platinum apparatus, add largely to the demand.

Perhaps the most serious and almost permanent loss of platinum is in the enormous consumption in dentistry, which is stated to account for over 60,000 oz. annually. An increasing amount is used in jewellery, and at least two-thirds of the large quantity employed in the lamp and other electrical industries is permanently lost. The platinotype process of photography and the use of platinum salts in the production of permanent colours for pottery, &c., also account for an increasing and very considerable permanent loss of the metal.

The power of absorbing gases, possessed by platinum has found a number of both purely scientific and commercial applications. Although massive platinum has the power of absorbing gases and is even porous to them, the value of the metal in this connection is mainly seen when it is in the form of spongy platinum or platinum black. Solid platinum will absorb 3·8 volumes of hydrogen gas at a red heat, and the gas will pass through platinum tubes at bright redness. The fact that many other gases and vapours are similarly adsorbed or occluded by this metal, has been taken advantage of in the glow-lamp of Davy and the lamp of Döbereiner. In each, the simultaneous occlusion of a combustible gas or vapour and oxygen from the air, brings the two into such intimate contact as to induce immediate combination. The heat of the combustion in the 'pores' of the metal, causes incandescence of the wire spiral in the case of the lamp of Davy or of the platinum sponge in the Döbereiner lamp.

By careful adjustment of the conditions, either complete or partial oxidation may be attained, and many oxidation processes may be carried out automatically with suitably prepared platinum. One of the earliest to be tried on the commercial scale was the conversion of alcohol into acetic acid.

The preparation of platinum sponge and platinum black for catalytic purposes, requires care and experience. For the manufacture of the former, the double chloride of platinum and ammonium is ignited to drive off the ammonium chloride and the chlorine combined with the platinum at the lowest possible temperature, so that the sponge shall retain the maximum surface; or asbestos, pumice, or other porous material may be saturated with platinum chloride and ignited, so that a still larger surface is exposed. Platinum black, a far more active form of the metal, is obtained as a finely divided residue, by treating alloys of platinum and soluble metals with dilute acids; or, better, by precipitating the platinum from a weak solution of the chloride with a reducing agent. Platinum black is capable of absorbing over 800 times its volume of oxygen, a portion of which appears to enter into combination as platinum hydroxide. It forms an extremely powerful oxidising or catalysing agent and is frequently used as such in organic chemistry, but it rapidly loses a portion of its activity and becomes denser and of the nature of spongy platinum.

The only large scale catalytic process in which platinum is employed, is the 'contact' process, in which sulphuric acid is manufactured direct from a mixture of sulphurous acid gas and air. This process, although long known, was not employed commercially until a demand arose for the strongest possible sulphuric acid for the manufacture of dyes, explosives, &c. The cost of evaporating the weak acid from the lead-chamber process or of preparing Nordhausen acid, and the increasing requirements of the trade led, however, to such improvements that 'contact' acid can be obtained of any necessary strength in terms of SO_3 dissolved in H_2SO_4 (*v.* SULPHURIC ACID).

The difficulties due to the rapid falling-off in the activity of the spongy platinum employed as the catalyser, have now been largely overcome, and the working up of the exhausted metal into fresh sponge has been simplified. The fact that arsenic rapidly 'sickens' the platinum, has rendered it necessary to remove that impurity from the sulphurous acid gas before oxidation, and the success which has attended such treatment has resulted in the production of acid remarkably free from arsenic and, at the same time, allowed the use of pyrites more arsenical than was previously permissible.

Such purification is largely effected by the use of iron oxide which, while removing arsenic with formation of ferric arsenate, oxidises much of the sulphurous acid. Many other catalysers have been employed with success, but none result in so complete a conversion of the sulphur dioxide into the trioxide and, even when they are employed, the aid of spongy platinum is generally required for the completion of the reaction.

The electrolytic action induced by the presence of a minute trace of platinum has a remarkable effect in promoting the solution of many metals in acid or other solvents, and in increasing their activity as reducing agents, &c. As platinum is so readily reduced by metals, the addition of a few drops of platinum chloride to the solution in which the metal lies, will often suffice for a large quantity of metal at a negligible cost, so that the application of this property which, although well known, has not yet been commercially employed, is well deserving of attention.

Although platinum can be readily alloyed with most metals, the alloys of industrial importance or even of scientific interest are few. As a rule, the qualities which render platinum valuable in the arts are destroyed by the presence of other metals, even in small quantities, and the addition of small quantities of platinum to other metals results in no improvement. The alloys of gold and platinum are of little importance, although of considerable interest on account of the fact that all bullion contains at least a trace of platinum, and that bullion is now largely treated electrolytically for its recovery in the United States and Germany. An alloy containing 70 p.c. of gold and 30 p.c. of platinum is only slightly yellow while, when more than 35 p.c. of platinum is present, no sign of yellow colour appears. Platinum and other platinum metals have a curious tendency to separate from their gold alloys, a fact which is noticeable when assaying gold bullion, where iridium, even when present in traces only, tends to pass to the bottom of the gold bead during cupellation. Matthey has pointed out that platinum concentrates towards the centre of an ingot cast from gold platinum alloys, so that great difficulty is experienced in the sampling of platiniferous bullion such as is obtained from many alluvial gold concentrates.

The platinum-silver alloys are of interest on account of their use in dentistry and, to some extent, as a solder for platinum, but mainly because the solubility of platinum so alloyed in nitric acid, and the insolubility in sulphuric acid, are utilised in the separation of platinum from gold and in the assay of ores supposed to contain platinum. For the latter purpose, an ordinary fire assay is performed exactly as for a gold ore, so that the platinum becomes collected in a button of lead together with any gold and silver which may be present. After the lead has been removed by cupellation, the silver may be removed (leaving the gold and platinum) by heating with sulphuric acid diluted with about one-fifth of its volume of water, or both the silver and platinum may be entirely dissolved (leaving the gold), by heating with dilute nitric acid. To ensure complete solution of the platinum in nitric acid, not less than 10 parts of silver to 1 of platinum must be present.

The alloys of platinum and iridium are of great value and of increasing importance. The presence of even a small quantity of iridium in platinum increases its hardness and generally adds to its resistance to heat and to corrosion by reagents. The alloy containing 10 p.c. of iridium has exceptional properties in these respects, and has been employed in the manufacture of standard weights and measures and, with pure platinum, for the thermo-couples of pyrometers. An alloy containing 10 p.c. of iridium was employed by Mr. George Matthey in preparing the standard measures of length for the International Standards Committee. He afterwards recommended a 15 p.c. alloy for that purpose, and a 20 p.c. alloy as the best for standard weights. Both show extremely high values for elasticity, malleability and ductility, and their uses are merely limited by their cost.

Although all the compounds which platinum forms with the non-metals are decomposed by heat and commonly also by reducing agents, this metal probably forms a larger and more interesting series of salts than any other of the noble metals, its double salts with the alkalis and alkaline earths being especially interesting.

G. T. H.

Platinum Compounds.

Oxygen compounds. Platinum monoxide PtO, which gives rise to the platinous salts, is formed as a grey powder when the hydroxide is ignited carefully; or as a violet powder by igniting calcium platinate and treating the residue with nitric acid. When heated strongly it yields the metal, and when reduced with formic acid it gives platinum black. It forms a stronger oxidising agent than the dioxide, and a better reducing agent than platinum (Wöhler, Zeitsch. anorg. Chem. 1904, 40, 423).

Platinous hydroxide $Pt(OH)_2$ may be formed by the action of caustic soda or potash on the dichloride, or, better, on aqueous potassium platinochloride. It is an oxidising agent and acts as a weak base, some of the salts of which have been prepared.

Platinum dioxide PtO_2 is a black powder obtained by heating the corresponding hydroxide.

Platinic hydroxide or **platinic acid** $H_2Pt(OH)_6$, or $PtO_2 4H_2O$ or $Pt(OH)_4 2H_2O$ (Bellucci, Atti. R. Accad. Lincei, 1903, [v.] 12, [ii.] 635; Gazz. chim. ital. 1905, 35, [ii.] 334; Blondel, Ann. Chim. Phys. 1905, [viii.] 6, 81), is prepared by boiling a solution of platinic chloride with caustic potash and treating the basic salt thus formed with acetic acid. When freshly prepared it is almost white, and is readily soluble in acids and alkalis, two of its hydrogen atoms being acidic and two basic. When dried, or on standing, it becomes yellow, and is no longer soluble in dilute acids. Platinic acid forms crystalline platinates of the type $M'_2Pt(OH)_6$, and also of a more complex constitution (Blondel, *l.c.*; Bellucci and Parravano, Atti. R. Accad. Lincei, 1905, [v.] 14, [i.] 459; Gibbs, Ber. 1877, 10, 1384; Herschel, Phil. Mag. 1832, [ii.] 1, 58).

The oxides Pt_3O_4, Pt_2O_3 have been described (Jörgensen, J. pr. Chem. 1877, [ii.] 16, 344; Dudley, J. Amer. Chem. Soc. 1902, 28, 59), but it is doubtful whether they really exist (Wöhler, *l.c.*). The *hydrated platinum sesquioxide*

$$Pt_2O_3,xH_2O,$$

intermediate between the two foregoing hydroxides, has been prepared by Wöhler and Martin (Ber. 1909, 42, 3958).

Platinum trioxide PtO_3 is formed when the hydrated dioxide is electrolysed in a 2N solution of potash at 0°. A brilliant golden-yellow substance of composition $3PtO_3,H_2O$ separates at the anode, and the trioxide can be isolated by neutralising the alkali with very weak acids. It forms a red-brown substance which loses oxygen readily, but is scarcely attacked by dilute mineral acids. Most reducing agents reduce it to platinum black. It liberates iodine from potassium iodide, but has little effect on alcohol, acetic acid, or many oxidisable organic substances. Many of the hitherto observed reactions of platinum are said to be due to the formation of this oxide (Wöhler and Martin, Ber. 1909, 42, 3326; *see* also Grube, Zeitsch. Elektrochem. 1910, 16, 621).

Halogen compounds. Platinum dichloride or **platinous chloride** $PtCl_2$ is formed by heating platinichloric acid H_2PtCl_6 to 300°, or by heating spongy platinum in a current of dry chlorine at 240°–250° (Schützenberger, Ann. Chim. Phys. 1870, [iv.] 21, 351). It is a greenish-grey insoluble powder, sp.gr. 5·87, which readily decomposes on heating into its elements (Shenstone, Chem. Soc. Trans. 1892, 450).

It readily combines with phosphorus trichloride, forming the compounds $PtCl_2,PCl_3$, $PtCl_2(PCl_3)_2$, the aqueous solution of which, when evaporated *in vacuô*, form *chloroplatino phosphorous acid* $PtCl_2P(OH)_3$ and *chloroplatino diphosphorous acid* $PtCl_2,2P(OH)_3$ respectively. The latter is decomposed at 12°, forming the white crystalline compound $PtClOP_2(OH)_5$, which at 150° is converted into a yellow powder $PtClO_2P_2(OH)_3$ (Schützenberger, Bull. Soc. chim. 1872, [ii.] 17, 428; *ibid.* 18, 153; Rosenheim and Löwenstamm, Zeitsch. anorg. Chem. 1903, 37, 394).

Platinous chloride combines with carbon monoxide, forming a number of carbonyl platinochlorides (Pullinger, Chem. Soc. Trans. 1891, 955).

Platinous chloride dissolves in hydrochloric acid, yielding platinochloric acid or chloroplatinous acid H_2PtCl_4, the potassium, other salts and compounds of which have been prepared (Thomsen, J. pr. Chem. 1877, [ii.] 15, 294; Nilson, *ibid.* 260; Magnus, Pogg. Ann. 1828, 14, 241; Klason, Ber. 1904, 37, 1360; Kurnakoff, J. Russ. Phys. Chem. Soc. 25, 565; Pigeon, Compt. rend. 1895, 120, 681).

Platinum tetrachloride or **platinic chloride** $PtCl_4$ is formed when platinum is heated in a current of chlorine (Troost and Hautefeuille, Compt. rend. 1887, 84, 946; Hodgkinson and Lowndes, Nature, May 3, 1888), or when dry platinichloric acid is heated in a current of chlorine or of hydrochloric acid (Pigeon, Compt. rend. 1890, 110, 77; *ibid.* 1891, 112, 1218; Ann. Chim. Phys. 1894, [vii.] 2, 433; Pullinger, *l.c.*). Hydrates containing 1, 4, 5, and 7 molecules of water have been prepared. In aqueous solution, the tetrachloride behaves as a weak dibasic acid $H_2PtCl_4(OH)_2$, and salts of this acid have been obtained (Miolati, Zeitsch. anorg. Chem. 1900, 22, 445; also Kohlrausch, Zeitsch. physikal. Chem. 1900, 33, 257; Hittorf and Salkowski, *ibid.* 1899, 28, 546; Dittenberger and Dietz, Ann. Chim. Phys. 1899, [ii.] 68, 853).

Platinum trichloride $PtCl_3$ has been obtained by Wöhler and Martin (*l.c.*) by heating platinic chloride in pure dry chlorine at 390° for 10 hours. It forms a dark green nearly black powder, soluble in boiling water, and decomposed by hot concentrated hydrochloric acid into the di- and tetra-chlorides.

A **platinum monochloride** PtCl has also been obtained (Sonstadt, Chem. Soc. Proc. 1898, 25, 179).

Platinichloric acid or **chloroplatinic acid** H_2PtCl_6 is prepared by dissolving platinum in *aqua regia* and evaporating with hydrochloric acid until all the nitric acid is removed. It may also be obtained by passing chlorine through concentrated hydrochloric acid containing platinum black in suspension; or by the electrolysis of platinum black (Weber, J. Amer. Chem. Soc. 1908, 30, 29: *see* also Matignon, Compt. rend. 1902, 134, 1497).

It crystallises with 6 molecules of water and forms reddish-brown deliquescent prisms. It readily yields crystalline salts of the type M'_2PtCl_6, known as the *platinichlorides* or *chloroplatinates*, of which the alkali salts are often used in analytical chemistry. It also forms characteristic salts with many organic compounds.

A number of chloroplatinic acids and their salts intermediate between platinic acid $H_2[Pt(OH_6)]$ and the hexachloro acid have been described (Bellucci and Miolati, Atti. R. Accad. Lincei, 1900, [v.] 9, ii. 51; *ibid.* 1902, [v.] 11, ii. 241, 271).

Platinous and platinic bromides and the corresponding acids (Meyer and Züblin, Ber. 1880, 13, 404; Halberstadt, *ibid.* 1884, 17, 2962: Bellucci, Atti. R. Accad. Lincei, 1900, v. 9, ii. 51), also the iodides and iodic acids (Bellucci, *ibid.* 11, i. 8; Pigeon, *l.c.*; Peterson, Zeitsch. anorg. Chem. 1898, 19, 59), the di-fluoride (Moissan, Compt. rend. 1889, 109, 807), and mixed halogen derivatives (Hertz, Ber. 1896, 29, 411) have also been prepared.

Nitrogen compounds. A number of metallic *platino nitrites* or *nitrito platinites* and their oxalo- and other derivatives have been described (Lang, J. pr. Chem. 1861, 83, 415; Blomstrand, *ibid.* 1871, [ii.] 3, 207; Nilson, Ber. 1876, 9, 1722; *ibid.* 1877, 10, 934; Vézes, Compt. rend. 1891, 112, 616; *ibid.* 113, 696; *ibid.* 1897, 125, 525: Bull. Soc. chim. 1901, [iii.] 25, 157; *ibid.* 1902, [iii.] 27, 930; *ibid.* 1903, [iii.] 29, 83; Berg, Zeitsch. anorg. Chem. 1897, 15, 278).

Fulminating platinum $(OH)_5PtNH_3Pt(OH)_5$ strongly resembles ferric hydroxide in appearance. It is prepared by treating hexachlorplatinic acid with silver nitrate in the cold. The silver hexachlorplatinate so formed is decomposed with hot water, and the resulting tetrachlorplatinic acid again treated with silver nitrate, and the new silver salt decomposed by boiling with water for some hours. The following reactions take place—

$$PtCl_6Ag_2+H_2O=Pt(OH)_2Cl_4H_2+2AgCl$$
$$Pt(OH)_2Cl_4Ag_2+H_2O=Pt(OH)_4Cl_2H_2+2AgCl$$

The solution of the dichloroplatinic acid treated with ammonia yields fulminating platinum, which when heated darkens, then detonates violently. A similar compound is obtained if pyridine is substituted for ammonia (Jacobsen, Compt. rend. 1909, 149, 574).

The various platinum salts form complex compounds with ammonia, similar in constitution to that of the chromium bases, and existing in two series in one of which the platinum is divalent, in the other tetravalent.

The chief types of platinous compounds are—

The platodiammines $[(NH_3)_4Pt]X_2$; platomonodiammines $[X(NH_3)_3Pt]X$; platosammine and platosemidiammine $[X_2(NH_3)_2Pt]$; and platosemiammine $[X_3(NH_3)Pt]R$. X and R = monovalent acid and basic radicles respectively.

The chief types of platinic compounds are represented by the following formulæ:—

$[(NH_3)_6Pt]X_4$; $[X_2(NH_3)_4Pt]X_2$; $[X_2(NH_3)_3Pt]X$; $[X_4(NH_3)_2Pt]$; $[X_5(NH_3)Pt]R$.

Magnus' green salt $Pt(NH_3)_4{\cdot}PtCl_4$, which was obtained by Magnus in 1828 (Pogg. Ann. 14, 204) by the action of ammonia on platinous chloride, is the starting-point for the preparation of all these derivatives. When boiled with ammonia it passes into *platodiammine chloride* or *tetrammine-platinous chloride* $[(NH_3)_4Pt]Cl_2$. The green salt may also be obtained by the action of potassium platinous chloride on platodiammine chloride, but if the solution is very dilute and neutral, or slightly ammoniacal, and traces of potassium platinichloride are absent, a rose-red crystalline salt is formed, which, when boiled with water passes into the green salt (Jörgensen and Sörensen, Zeitsch. anorg. Chem. 1906, 48, 441).

Literature.—Gras, Ann. Chim. Phys. [ii.] 69, 204; Peyronne, *ibid.* 1844, iii. 12, 193; 1846, [iii.] 16, 462; Reiset, *ibid.* 1844, [iii.] 11, 417; Compt. rend. 1844, 18, 1103; Schou, Zeitsch. anorg. Chem. 1896, 13, 36; Kurnakoff, *ibid.* 1898, 17, 207; Klason and Wauselin, J. pr. Chem. 1903, [ii.] 67, 41; Euler, *ibid.* 1904, 37, 2391; Tarugi, Gazz. chim. ital. 1906, 36, i. 364; Ray and Shosh, Zeitsch. anorg. Chem. 1909, 64, 184; Werner, Ber. 1907, 40, 4093; Jörgensen and Sörensen, *l.c.*; and many others). Organic derivatives of ammonia compounds have been described by Klason (J. pr. Chem. 1903, [ii.] 67, 1; Jörgensen, Zeitsch. anorg. Chem. 1906, 48, 374).

Platinum compounds of *hydroxylamine* have been described by Uhlenhuth (Annalen, 1900, 311, 120), and an explosive *potassium platinoazoimide* by Curtius and Rissow (J. pr. Chem. 1898, [ii.] 58, 261).

Platinocyanic acid $H_2[Pt(CN)_4]$ is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen or the barium salt with dilute sulphuric acid (Quadrat, Annalen, 1849, 70, 300; Weselsky, J. pr. Chem. 1856, 69, 276). When crystallising with 5 molecules of water it forms fine cinnabar-red prisms exhibiting a brilliant blue colour by reflected light; when containing more water the crystals have a yellow-green colour with a golden lustre.

Platinocyanides may be prepared by dissolving well-washed freshly-prepared platinum sulphide in a solution of the corresponding cyanide.

The colourless solution is then concentrated. The reaction proceeds thus :

$$PtS_2+5KCN=K_2Pt(CN)_4+K_2S+KCNS$$

(Schertel, Ber. 1896, 29, 204) ; or they may be prepared by double decomposition from the potassium salt which is formed by heating spongy platinum with potassium ferrocyanide to redness, or by dissolving platinous chloride in potassium cyanide (Knopp, Annalen, 1842, 43, 111). The platinocyanides are characterised by their reaction with the mercury salts with which they first give a white precipitate, which on addition of more mercury salt turns blue. They become luminous when exposed to Röntgen rays, and are used for making screens for the detection of these rays.

Nearly all platinocyanides fluoresce to a marked degree, the colour and intensity of fluorescence depending on the character of the basic radicle, the state of hydration, the perfection of the crystalline forms, and in some cases on the mode of preparation. Certain of the platinocyanides exist in two modifications, having the same crystalline form, but, prepared by different methods, they show a difference in all their optical characteristics. It is remarkable that *uranyl* platinocyanide displays no fluorescence, although each of their constituents confers this property on most salts (Levy and Sisson, Chem. Soc. Trans. 1906, 125 ; Levy, *ibid.* 1908, 1446 ; also Jackson, *ibid.* 1896, 57).

Some further literature, Bergsöe, Zeitsch. anorg. Chem. 1899, 19, 318 ; Brochet and Petit, Compt. rend. 1904, 138, 1095 ; Reynolds, Proc. Roy. Soc. 1909, 82, A, 380. Dicyanodiamidinium platinic chloride $(C_2H_6N_4O)_2PtCl_6$ is described by Grossmann and Schück (Ber. 1910, 43, 674).

For thiocyanates, *see* Buckton, Chem. Soc. Trans. 1855, 22 ; Miolati and Bellucci, Gazz. chim. ital. 1900, 30, ii. 588 ; Grossmann and Schück, Ber. 1906, 39, 1896.

Sulphur compounds. Platinum monosulphide PtS forms a green powder or glistening needles, prepared by heating platinum sponge with sulphur in a vacuous glass tube (Debray and Deville, Compt. rend. 1879, 89, 587).

Platinum disulphide PtS_2 may be obtained pure as a steel-grey powder by precipitating a 3 p.c. solution of potassium platinichloride at 90° with sulphuretted hydrogen. At ordinary temperature, a yellowish-brown precipitate is formed, while the liquid becomes red, containing colloidal platinum sulphide, which is deposited at 0° (Antony and Lucchesi, Gazz. chim. ital. 1896, 26, i. 211).

Platinic sulphate $Pt(SO_4)_2,4H_2O$ forms large orange leaflets (Stuchlik, Ber. 1904, 38, 2913).

A number of *thio* platinum salts have been prepared (Schneider, Pogg. Ann. 1866, 138, 604 ; J. pr. Chem. [ii.] 48, 411 ; Hofmann and Höchtlen, Ber. 1903, 36, 3090). *Tellurides* Pt_2Te, $PtTe_2$, PtTe (Roessler, Zeitsch. anorg. Chem. 1897, 15, 405), and *selenides* PtSe, $PtSe_2$, $PtSe_3$ (Roessler, *ibid.* 1895, 9, 59 ; Minozzi, Atti. R. Accad. Lincei, 1909, v. 18, ii. 150) also exist.

A platinum compound analogous to purple of Cassius (*v.* GOLD PURPLE) is obtained by the action of stannous chloride on solutions of platinum salts, when a blood-red solution is formed, which darkens after a time, particularly on warming, finally becoming black and slightly turbid. When shaken with ether or ethyl acetate the red colour is extracted, and on addition of water, a chocolate-brown precipitate is formed, consisting of platinum, tin, and oxygen in varying proportions. When freshly precipitated it is soluble in hydrochloric acid. It does not diffuse through parchment paper, and may be regarded as an adsorption compound of colloidal platinum and colloidal stannic acid, but the former shows none of the ordinary reactions of colloidal platinum. A similar red solution has been obtained by reducing platinic chloride with an ethereal solution of phosphorus in the presence of gelatin (Wöhler, Verh. deut. Naturforch. Aerzte, 1907, ii. 105 ; Wöhler and Spengel, Zeitsch. Chem. Ind. Kolloide, 1910, 7, 243).

Platinum phosphides PtP_2, Pt_3P_5 (Granger, Compt. rend. 1896, 123, 1284), **platinic pyrophosphate** PtP_2O_7 (Barnett, Chem. Soc. Trans. 1895, 513), *arsenides* $PtAs_2$ and the *arsenite* $Pt_3(AsO_3)_4$ (Stavenhagen, J. pr. Chem. 1895, [ii.] 51, 1) ; the *silicides* SiPt, $SiPt_2$ (Vigouroux, Compt. rend. 1896, 123, 115 ; *ibid.* 1907, 145, 376) ; and also *tungstates* and *molybdates* of platinum (Gibbs, Amer. Chem. J. 1895, 17, 73) have been prepared.

Organic compounds of platinum. Alkyl compounds of platinum may be prepared by the interaction of magnesium methyl iodide and platinic chloride, a number of these substances and their hydroxide, nitrate, sulphate, chloride, cyanide, and platinocyanide derivatives have been prepared by Pope and Peachy (Chem. Soc. Trans. 1909, 571).

Platinous xanthate $(OEt{\cdot}CS{\cdot}S)_2Pt$ occurs in flat yellow prisms, m.p. 129°–130°, is insoluble in water, but readily soluble in chloroform.

Other platinous salts of thio-organic acids are described by Ramberg (Zeitsch. anorg. Chem. 1906, 50, 439).

Complex *platino pyridine halides* are described by Jörgensen and Werner, *ibid.* 1896, 12, 46 ; *ibid.* 1900, 25, 353 ; Klason, Ber. 1904, 37, 1349.

Organic phosphorus platino halides by Rosenheim and Levy (Zeitsch. anorg. Chem. 1905, 43, 34).

Platinum alginate is a brown gelatinous precipitate readily soluble in ammonia, forming a yellow solution (Stanford, J. Soc. Chem. Ind. 1886, 220).

For certain other organic compounds, *see* Werner, *l.c.* ; Corsa, Gazz. chim. ital. 22, ii. 620 ; Hofmann and Rabe, Zeitsch. anorg. Chem. 1897, 14, 293 ; Prandtl and Hofmann, Ber. 1900, 33, 2981 ; H. and Bugge, *ibid.* 1908, 41, 312 ; H. and Narbutt, *ibid.* 1625 ; H. and Buchner, *ibid.* 1909, 42, 3392 ; Tschugaeff and Sokoloff, *ibid.* 55 ; Ostromisslensky and Bergmann, *ibid.* 1910, 43, 2768.

PLUM, *Prunus spp.* Many species and varieties are known. As the average of 33 analyses, König gives for the composition of the fruit—

Water	Protein	Free acid (Malic)	Sugar	Other N-free ext.	Fibre and stone	Ash
78·6	1·0	0·8	8·8	4·0	5·8	0·5

For analyses of Californian grown plums and prunes *v.* Colby (Experim. Stat. Rec. 1893, 4, 918), who found the juice of plums to contain about 18 p.c. of sugar and 0·5 p.c. free acid (as H_2SO_4).

The kernel contains amygdalin and emulsin; it is also rich in a fixed oil. The rind contains a wax melting at 64° (Seifert, Landw. Versuchs. Stat. 1894, 45, 29). Plums require and remove from the soil far larger quantities of nitrogen than are demanded by most other orchard crops, *e.g.* apples or pears. According to American estimates, an average crop of plums (30,000 lbs. per acre), removes about 127 lbs. of nitrogen, 13 lbs. phosphoric acid, and 51 lbs. of potash per acre from the soil, while for apples and pears (each 20,000 lbs. per acre), the figures are 12 and 12 lbs. of nitrogen, 6 and 10 lbs. phosphoric acid and 16 and 36 lbs. potash respectively.

For effect of manuring upon the yield of plums and damsons *v.* Dyer and Shrivell (Jour. Roy. Hort. Soc. 1903, 27, part 4). H. I.

PLUMBAGO *v.* Graphite.

PLUMIERIDE *v.* Agoniada bark.

PLUMOSITE *v.* Feather-ore.

PODOPHYLLIC ACID, PODOPHYLLOQUERCETIN, and **PODOPHYLLOTOXIN** *v.* *Podophyllum resin*, art. Resins.

PODOPHYLLUM RESIN *v.* Resins.

POLARIMETRY.

I. Qualitative.

When a ray of light falls on the surface of an isotropic substance like glass, it is, in general, bent out of its path at the surface of separation of the two media, according to a law discovered by Snellius in 1621. The incident and refracted rays lie in the same plane with the normal to the surface at the point of incidence, the sine of the angle of incidence divided by the sine of the angle of refraction being a constant.

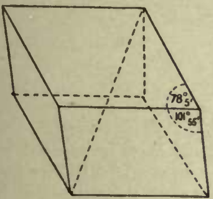

Fig. 1.

In 1669, Bartholinus noticed that if a ray of light enters a crystal of Iceland spar, it splits, usually, into two rays, one of which pursues its way through the crystal according to the ordinary laws of refraction, whilst the behaviour of the other depends upon the direction of the original beam relative to the crystal face. The fundamental form of Iceland spar is the rhombohedron, Fig. 1, and if the edges of the rhomb be equal, the line joining the obtuse solid angles is the crystallographic axis. If the rhomb is not equal edged, the axis is any line parallel to this direction.

If a mark on white paper be examined through a crystal of Iceland spar, whose refracting face is parallel with the paper, two images will be seen. On turning the crystal about a vertical axis, one of these remains fixed whilst the other moves round it, a line joining the two images being always in the direction of the shorter diagonal of the face of an equal edged crystal. The plane passing through this direction perpendicular to the face of the crystal contains the optic axis and is called the principal plane, the images being termed, respectively, ordinary and extraordinary. A ray incident on a surface cut parallel to the optic axis splits into two rays, each following the laws of single refraction but with a different refractive index, and when the ray is incident normally to the surface, the two rays coincide in direction but move through the crystal with velocities inversely proportional to their refractive indices, $\mu_o=1{\cdot}654$, $\mu_e=1{\cdot}483$.[1] Generally, however, the extraordinary ray is neither in the same plane with the normal and the incident ray, nor is $\frac{\sin i}{\sin r}$=a constant. If the crystal in the above experiment be tilted at different angles, it will be noticed that the separation of the images varies, and when the light travels through the crystal in the direction of the optic axis there is again no separation, both rays pursue the same path with exactly the same velocity.

The theory of the propagation of these two wave-fronts was developed by Huyghaens, who discovered (1690) that both rays differ markedly from the original beam, for, if passed into another crystal situated similarly to that in which they were produced, they are not further resolved, the ordinary ray passes through as an ordinary, and the extraordinary as an extraordinary ray. If, however, their refracting faces being kept parallel, one crystal be turned through an angle of 90° relative to the other, the ordinary ray from the first passes through the second as an extraordinary and the extraordinary as an ordinary ray. In intermediate positions both rays are divided. Newton suggested that these rays have ‘sides’ (Optics, 1704, Queries 25, 26), meaning thereby that their properties vary in different directions, but the matter attracted little or no attention until after the lapse of another century, when Malus discovered, in 1808, that light could be brought into this peculiar condition by reflection as well as by refraction (Nouv. Bull. Soc. Philom. 1807–9, 1, 266, 341, 353; 1810–11, 2, 252, 291, 320; Gilbert's Ann. 1812, 40, 119, 132).

If a beam of light fall upon a sheet of glass, an angle of incidence of about 55° 25′ [2] giving the maximum effect, part will be reflected and part refracted. Both rays are found to have ‘poles,’ as Malus put it, and, if allowed to traverse a piece of Iceland spar, whose refracting face is perpendicular to the plane of incidence and whose principal plane is parallel to the plane of incidence, the reflected beam will pass through as an ordinary ray. The refracted ray under these circumstances will pass through as an extraordinary ray. The plane of incidence of the light on the reflecting surface came to be called the *plane of polarisation*.

The theory of the subject is due to Fresnel who, in connection with the phenomena of interference which had been discovered by Young, had just developed the transverse wave theory of light. He explained the difference between the ordinary and the extraordinary rays in Iceland spar by the supposition that, whilst the vibrations of the ether particles causing the ordinary ray take place in one plane only, those causing the extraordinary ray occur in a plane at right angles to the first, and he showed that, on his hypothesis, the vibrations of light reflected from a surface at the polarising angle take place in a plane parallel to the surface and therefore at right angles to what was called the plane of polarisation (Nouv. Bull. Soc. Philom. 1824, 9, 150; Ann. Chim. Phys. 1821, 17, 186).

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[1] The double refraction of Iceland spar is said to be negative. The double refraction of quartz is positive, the indices being $\mu_o=1{\cdot}544$, $\mu_e=1{\cdot}553$.

[2] The angle varies with the index of refraction of the glass.

According to the modern electro-magnetic theory of light as developed by Clerk Maxwell, there is a magnetic disturbance *in* the plane of polarisation and an electric disturbance *perpendicular* to it. The latter, therefore, corresponds with Fresnel's vibrations.

In 1811, Arago discovered the phenomenon of the rotation of the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1810–1811, 2, 358, 371, 387; Gilb. Ann. 1812, 40, 145). A ray reflected from a piece of glass at the proper angle was received upon a crystal of Iceland spar. It then splits in general into two rays of unequal intensity, and, if the crystal be turned round the direction of the ray as axis, four positions will be found, at right angles, in which only one image appears, alternately ordinary and extraordinary. When the crystal is set in one of these positions, and a piece of quartz, cut perpendicular to the axis AA′ (Fig. 2), is placed in the path of the ray between the polarising mirror and the crystal, two images appear, complementary in colour—the colours depending on the thickness of the plate—and, if they happen to overlap, the part common to both is white. On turning the crystal the colours change. Something of a similar kind was found for mica and gypsum.

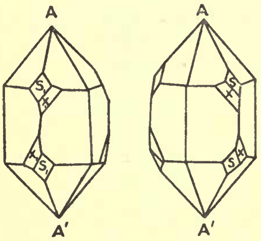

FIG. 2.

Arago recognised that passage through the quartz plate altered the plane in which the light was polarised, and that the colours were due to the fact that the planes of polarisation of the different rays of which white light is composed, are rotated to different extents.

Biot then found (Mém. de l'Institut, 1812, Part I. 218) that the rotation conferred on the plane of polarisation was proportional to the thickness of the plate, and varied with the refrangibility of the light used, the red rays being least rotated and the violet the most, some crystals rotating to the right, others to the left. Later, while engaged on experiments which necessitated the immersion of crystalline plates in liquids to make the polarised rays penetrate the plates very obliquely to the surface, he discovered some of these liquids also to be capable of rotating the plane of polarisation of light (Nouv. Bull. Soc. Philom. 1814–15, 4, 190). This was the case for oil of terebenthine (*l*-pinene, French oil of turpentine) and oil of laurel, each of which always turned the plane of polarisation from right to left, whilst oil of citron, and camphor dissolved in alcohol had the opposite effect. Experiments of a somewhat similar character were carried out by Brewster from about 1812, *e.g.* Phil. Trans. 1815, [i.] 29, and T. J. Seebeck (Schweigger's Journal, 1813, 7, 259, 382; 1814, 12, 1; Nouv. Bull. Soc. Philom. 1816, 5, 49). Subsequently Biot determined the effect of temperature change on the rotation of oil of terebenthine, examined the influence of solvents, discovered the rotation of cane sugar, applied the polarimetric method to distinguish between natural and artificial camphor and even ascertained that oil of terebenthine in the state of vapour, still retains its rotation[1] (Ann. Chim. Phys. 1818, [ii.] 9, 377; 1819, [ii.] 10, 68).

Fresnel, after discovering circularly polarised light, showed that the rotation of the plane of polarisation of light by quartz cut perpendicular to the axis, could be explained, if on entering the quartz the polarised beam were resolved into two circularly polarised rays travelling through the crystal in the direction of the optic axis, without separation but with different velocities. Then, on emergence, there would be a difference of phase so that the two waves recombine to form again a plane polarised ray whose plane of polarisation is, in general, not that of the original beam. He succeeded in demonstrating the actual existence of these two circularly polarised rays, the principle of his method, if not the actual arrangement of his apparatus, being represented by Fig. 3. ABC and CDE are prisms of lævo- and BCD one of dextro- quartz, so cut that the optic axis of each is parallel to BD. Now let a ray of plane polarised light[2] fall normally on the surface AB at F, and suppose that it splits into two circularly polarised rays which travel in the direction FG. That whose path is a right-handed helix should travel with a greater velocity in the lævo prisms ABC and CDE than in the dextro prism BCD. In passing through the system, therefore, this ray should be bent towards the normal at G, and away from it at M and also at N. Similarly, the ray whose path is a left-handed helix should travel more slowly in ABC and CDE than in BCD and be bent away from the normal at G, towards it at H, and away from it at K. The two rays therefore emerge in the directions NO and KL. This separation was actually observed, although it was very small, and the two rays were found to be circularly polarised in opposite senses (Ann. Chim. Phys. 1825, 25, 147). Fresnel explained the rotation of liquids in the same way but the experimental demonstration was made much later by v. Fleischl, whose method was similar to that of Fresnel, dextro- and lævo-rotatory liquids of the same refractive index being placed alternately in hollow glass prisms (Sitzungsber. Wien. Akad. 1884, 90, ii. 478).

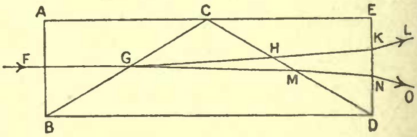

FIG. 3.

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[1] It may be mentioned here that if the ray be reflected back through the tube of active substance, the rotation conferred on the plane of polarisation during the first passage is annulled during the second, the light emerging polarised in the original plane. *Cf.* p. 331.

[2] Ordinary light gives the same result.

Although Biot had found that some quartz crystals are dextro- and others lævo-rotatory, he was unable to suggest any property of the quartz—instancing crystalline form—which could be correlated with the phenomenon of rotation, but Herschel (Trans. Camb. Phil. Soc. 1821, 1 [i.] 43), remarking that the experiments of Biot gave the impression 'of a want of symmetry in the disposition within the molecules themselves, of some of the elementary forces by which they act on light' (p. 43), pointed out that an indication of this want of symmetry had already been discovered by Haüy in the plagiehedrism or hemihedrism which shows itself in quartz by the presence of the little facets marked x and x′ in Fig. 2,[1] which in some crystals lean towards the right and in others towards the left. Plates cut from a crystal showing facets leaning towards the left, all rotated the plane of polarisation 'to the left, to an observer looking in the direction of the ray's progressive motion, or to the right of one receiving the ray in his eye' (p. 48). At the present time it is conventional to define the sign of rotation in the latter way so that his specimen was what is now called dextro-rotatory. In every other crystal examined the rotation was in the sense that would be expected from the position of the facets.

Some twenty years later, this discovery had a most important influence on Louis Pasteur, who, in 1841, repeated, for practice in crystallography, a research published by de la Provostaye (Ann. Chim. Phys. 1841, [iii.] 3, 129) on the crystal forms of tartaric acid, paratartaric acid (racemic acid), and their salts, in regard to which it had been observed by Biot that tartaric acid is optically active (Mém. de l'Acad. 1835, 13, 46) whilst racemic acid is inactive (Ann. Chim. Phys. 1838, [ii.] 69, 22). In this work (*ibid.* 1848, [iii.] 24, 442) he noticed something overlooked by de la Provostaye, namely that all the tartrate crystals had hemihedral facets, although they were not always very distinct, whereas racemic acid and such of its salts as he examined showed no hemihedrism. He also observed that the ratio of two of the axes in the tartrates is nearly the same, whilst the third differs considerably, and, if crystals of different tartrates be similarly situated, the arrangement of the hemihedral facets is always in the same sense. It then occurred to him that the relationship which had been inferred by Herschel for quartz might also apply in the case of the tartrates. Just about this time, Mitscherlich stated that: 'Sodium ammonium tartrate and sodium ammonium racemate have the same chemical constitution, the same crystal form with the same angles, the same specific gravity, and the same double refraction, in consequence of which their optic axes are inclined at the same angle; . . . the nature and number of the atoms, their arrangement and their distance from each other are the same in both compounds,' and yet tartaric acid in solution rotates the plane of polarisation of light whilst dissolved racemic acid is indifferent (Monatsber. der Berl. Akad. 1842; Compt. rend. 1844, 19, 720). Pasteur, thinking it possible that Mitscherlich, like de la Provostaye, had overlooked the presence of hemihedral facets which might be expected on the tartrate but not on the racemate, then investigated these salts, which were not among those he had already examined. As he expected, the tartrate was indeed hemihedral, but, to his surprise, the racemate was hemihedral also. On closer examination, however, he noticed that whereas the facets on the tartrate crystals all occurred in the same position, in the racemate they appeared, sometimes towards the right, sometimes towards the left. Doubtless still guided by Herschel's idea, he picked out from the mass some of each kind of crystal and when dissolved separately in water one sort gave a dextro-rotatory and the other a lævo-rotatory solution. Fig. 4 shows the appearance of these crystals whose formula is

$$Na(NH_4)C_4H_4O_6,4H_2O.$$

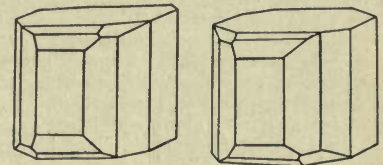

Fig. 4.

Racemic acid thus appeared as a compound or a mixture of a peculiar kind perhaps, of ordinary tartaric acid with another variety of tartaric acid, similar in every respect except its rotation and the shape of its crystals which were exactly equal although opposite in sense. Racemic acid, however, does not separate, under any conditions at present known, into the two different forms, and indeed it is only by crystallising it within narrow limits of temperature that sodium ammonium tartrate will separate from solution in the two different forms. Herschel had already a distinct idea of a relationship between asymmetrical crystal structure and optical rotation and the idea was much developed by Pasteur as regards the chemical molecule. He pointed out that many of the objects with which we are acquainted can be separated into two classes: those which are superposible on their mirror images and those that are not. Thus the human body as a whole and apart from minor irregularities, a straight stair, a regular tetrahedron, are identical with their mirror images. But the mirror image of a right hand or of a left hand, of a spiral stair, of an irregular tetrahedron, although each is similar to its object, is not superposible on it; cannot, in the language of Euclid, be similarly situated; the image of a right hand is a left hand. The molecules of the two forms of tartaric acid Pasteur supposed to differ in the same way; the image of a dextro-rotatory molecule is a lævo-rotatory molecule. They would not then be expected to vary in regard to symmetrical forces or properties; they would have the same solubility, the same density, the same amount of water of crystallisation—or lack of it—the same melting-point, the same strength, and in many of their reactions they would behave alike, with ethyl alcohol or sodium hydroxide, for example. But with respect to certain other forces, presumably unsymmetrical, they behave exactly in opposite senses—whilst one rotates the plane of polarisation of light by a definite amount in one direction, the other rotates it by just the same amount in the opposite direction.

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[1] The figure given by Herschel is incorrect. It represents a twin which, presumably, would have no rotation.

Pasteur further foresaw that by combining each of a pair of enantiomorphously related molecules with one form of some other active molecule, figures should be obtained which would no longer be completely enantiomorphic. Thus, for instance, if a right-handed and a left-handed spiral of equal dimensions be each combined with a right-handed spiral of a different diameter, the two compound figures will not be enantiomorphously related. Compounds such as they may be supposed to represent, need not be expected to show an identical behaviour even towards symmetrical forces. They might not have the same melting-point, for instance, or the same solubility. This Pasteur found to be the case. He prepared cinchonicine hydrogen racemate and on allowing the solution to evaporate, the acid salt of cinchonicine with lævo-tartaric acid separated first, afterwards the corresponding salt of cinchonicine with dextro-tartaric acid also crystallised out. The two were quite different in appearance, in solubility, in melting-point, and from them the two different acids could be obtained. Thus Pasteur introduced that method which, since his time, has been used more than any other for the resolution of substances similar in character to racemic acid.

Pasteur carried his investigation a step further. It was known that commercial calcium tartrate occasionally fermented, with the formation of various products. He imitated this fermentation, first with ammonium tartrate, which was destroyed, and then with ammonium racemate. In the latter case, the liquid, originally inactive, gradually became lævo-rotatory, and from it could be obtained ultimately lævo-tartaric acid. The micro-organisms had destroyed the dextro-acid, leaving the lævo-isomeride behind. Here, again, Pasteur established another method of a general character for the resolution of substances of the type of racemic acid. (For a fuller account of these researches *see* Alembic Club Reprints, No. 14, W. F. Clay, Edinburgh; also Pasteur Memorial Lecture, P. F. Frankland, Chem. Soc. Trans. 1897, 71, 683).

Even this brilliant work, however, supplied no criterion to decide which chemical compounds were similar in character to racemic acid, and might therefore be expected to yield dextro- and lævo- isomerides, while theoretical organic chemistry was not at that time sufficiently developed to render possible a correlation of rotatory power with the constitution of naturally occurring active substances. Some twenty years had to elapse before this became possible, the work of Pasteur being the incentive to one attempt to overcome the difficulty, the investigations of Wislicenus on the various forms of lactic acid and the speculations of Kekulé having much to do with another.

As Wislicenus pointed out, the plane formulæ in use about 1870 were insufficient to explain the existence of the three known lactic acids, and he suggested that this subtle isomerism might perhaps be represented by different spatial arrangement of the atoms of the molecules. Paralactic acid and fermentation lactic acid were probably only geometric isomerides (Ber. 1869, 2, 550, 620; Annalen, 1873, 67, 343).

In 1874, van 't Hoff (in a pamphlet) and Le Be (Bull. Soc. chim. 1874, [ii.] 22, 337) published practically identical views, referring the asymmetry which Pasteur had attributed to the molecule of an active compound as a whole to one or more of its carbon atoms. If a carbon atom be combined with four different atoms or groups, and it be assumed that the affinities of the carbon atom are directed towards the angles of a tetrahedron, it is possible to arrange the four groups in two different ways such that the mirror image of the one arrangement is identical with the other arrangement (Fig. 5). Further, such compounds as were known to be optically active, contained carbon atoms of the above character, whence it might be inferred that any inactive compound containing an asymmetric carbon atom should be capable of resolution into active isomerides.

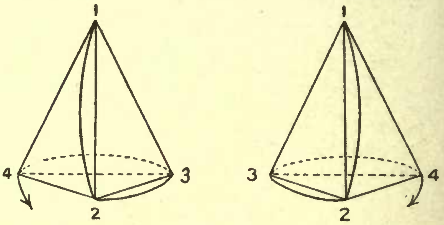
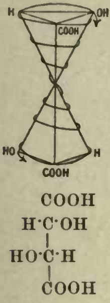


FIG. 5.

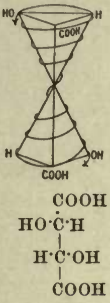
This idea explained all that Pasteur had discovered about tartaric acid. The constitutional formulæ then coming into use, exhibited the presence of two asymmetric carbon atoms in the substance, and by combining two such atoms in different ways it was possible to account for all the existing isomerides. Thus, in Fig. 6, the grouping of the radicles about the upper carbon atom is the same as that about the lower one, and since both the radicles of which the molecule is composed are the same in configuration, the molecule should be active, say in a *dextro* sense. Fig. 7 shows a molecule composed of two radicles each of opposite asymmetry to those of Fig. 6, and should therefore represent *lævo*-tartaric acid. A mixture of equal numbers of these molecules will constitute racemic acid, which is capable of resolution into the two active forms, whilst, if two radicles of opposite asymmetry be combined, as in Fig. 8, the molecule obtained should be inactive, because the two parts of which it is composed tend to turn the plane of polarisation of light equally in opposite directions, and, at the same time, it should not be capable of resolution since all the molecules composing it are exactly the same. This is the *meso*-tartaric acid of Pasteur. The spirals drawn round the asymmetric atoms and passing through the groups always in the same sequence, help to show that the twist given to the plane of polarisation of light is in the same sense whichever end of the molecule the ray enters at. The lower formulæ of the Figs. 6, 7, 8, show the conventional method of projecting these three dimensional figures on to the plane of the paper.

The work carried out on optical activity since the publication of the views of van 't Hoff and Le Bel has been, for the most part, a splendid confirmation of them, but, in some directions, there have been developments. It has been shown that carbon is not the only element that can give rise to optical activity. In the case of nitrogen, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1127) were successful in resolving benzylphenylallylmethylammonium iodide by means of *d*-camphorsulphonic acid (*see also* Pope and Read, *ibid.* 1912, 101, 519), and later, H. O. Jones (*ibid.* 1903, 83, 1418; 1904, 85, 223) resolved phenylbenzylethylmethylammonium iodide (*see also ibid.* 1906, 89, 280). Compounds owing their activity to the presence of an asymmetric tin atom were obtained by Pope and Peachey (Chem. Soc. Proc. 1900, 16, 12), others containing asymmetric sulphur by Pope and Peachey (Chem. Soc. Trans. 1900, 77, 1072), and Smiles (*ibid.* 1900, 77, 1174), asymmetric selenium by Pope and Neville (*ibid.* 1902, 81, 1552), asymmetric silicon by Kipping (*ibid.* 1907, 91, 209; 1908, 93, 2090), asymmetric phosphorus by Meisenheimer and Lichtenstadt (Ber. 1911, 44, 356), and Kipping and Challenger (Chem. Soc. Trans. 1911, 99, 626), and even asymmetric cobalt (Ber. 1911, 44, 1887) and chromium (*ibid.* 1912, 45, 865) by Werner.



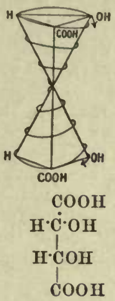
$$\begin{array}{c} \mathrm{COOH} \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{HO{\cdot}C{\cdot}H} \\ | \\ \mathrm{COOH} \end{array}$$

FIG. 6.



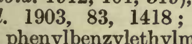
$$\begin{array}{c} \mathrm{COOH} \\ \mathrm{HO{\cdot}\dot{C}{\cdot}H} \\ | \\ \mathrm{H{\cdot}C{\cdot}OH} \\ | \\ \mathrm{COOH} \end{array}$$

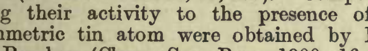
FIG. 7.



$$\begin{array}{c} \mathrm{COOH} \\ \mathrm{H{\cdot}\dot{C}{\cdot}OH} \\ | \\ \mathrm{H{\cdot}COH} \\ | \\ \mathrm{COOH} \end{array}$$

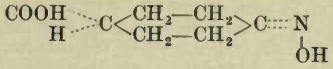
FIG. 8.

Pasteur attributed the rotation of chemical compounds to the asymmetry of the molecule as a whole and van 't Hoff pointed out, in 1877 (The Arrangement of Atoms in Space, 1898, 103), that a compound derived from allene of the formula  ought to exist in two enantiomorphic and therefore, active forms, because if *a*, *b*, and the bonds joining them to their carbon atom lie in the plane of the paper, *c*, *d*, and their bonds must lie in a plane perpendicular to the first, so that a tetrahedron could be laid through the points, *a*, *b*, *c*, *d*. Thus optical activity might exist in a compound containing no asymmetric carbon atom as defined by van 't Hoff. Attempts to prepare such substances failed until Perkin and Pope succeeded in synthesising *l*-methyl*cyclo*-hexylidene-4-acetic acid



$$\begin{array}{l}\mathrm{CH_3}\\\mathrm{H}\end{array}\!\!>\mathrm{C}<\begin{array}{l}\mathrm{CH_2{-}CH_2}\\\mathrm{CH_2{-}CH_2}\end{array}\!\!>\mathrm{C}{=}\mathrm{C}<\begin{array}{l}\mathrm{H}\\\mathrm{COOH}\end{array}$$

(which is not exactly of the above type) and this was later resolved into its two components by crystallisation of the brucine salt from dilute alcohol (Perkin, Pope and Wallach, Chem. Soc. Trans. 1909, 95, 1789; *see also* Perkin and Pope, *ibid.* 1911, 99, 1510). A compound the asymmetry of which is of the same kind is 4-oximino*cyclo*-hexanecarboxylic acid



$$\begin{array}{l}\mathrm{COOH}\\\mathrm{H}\end{array}\!\!>\mathrm{C}<\begin{array}{l}\mathrm{CH_2{-}CH_2}\\\mathrm{CH_2{-}CH_2}\end{array}\!\!>\mathrm{C}{=}\begin{array}{c}\mathrm{N}\\|\\\mathrm{OH}\end{array}$$

(Mills and Bain, Chem. Soc. Trans. 1910, 97, 1866), but the claim that these compounds really contain no asymmetric carbon atom has been disputed by Everest (Chem. News, 1909, 100, 295; Chem. Soc. Proc. 1911, 27, 285), and Marsh (*ibid.* 1911, 27, 317; *see also* P. F. Frankland, Chem. Soc. Trans. 1912, 101, 655).

Additional Methods for producing Optically Active Compounds.

To Pasteur's three methods for obtaining optically active compounds there may be added some others. Marckwald and McKenzie found (Ber. 1899, 32, 2130) that when mandelic acid was heated with menthol for an hour at 155°, the mandelic acid which remained unacted on, contained a greater proportion of the lævo- than of the dextro- constituent, and on this fact a method can be based for separating them.

Again, when an inactive substance, whilst in combination with an active compound, is submitted to some reaction which produces in it an asymmetric carbon atom, it often happens that one arrangement of the groups around this new asymmetric atom is produced in preference to the other. The new asymmetric molecule can then be separated from the one originally active. Thus, for example, by reduction of *l*-menthyl pyruvate $CH_3{-}CO{-}CO{\cdot}OC_{10}H_{19}$, *l*-menthyl lactate $CH_3{-}CH(OH){-}CO{\cdot}OC_{10}H_{19}$, was obtained (McKenzie, Chem. Soc. Trans. 1905, 87, 1373), and the lactic acid separated from this was found to be slightly lævo-rotatory. By such processes of *asymmetric synthesis*, McKenzie has produced other active compounds (*ibid.* 1904, 85, 1249; 1905, 87, 1004; 1906, 89, 365).

An ingenious asymmetric synthesis was also carried out by Marckwald, by heating the acid brucine salt of methyl-ethyl-malonic acid, when valeric acid was obtained containing a slight excess of the lævo-isomer (Ber. 1904, 37, 4696). These methods are, however, meanwhile only of theoretical interest.

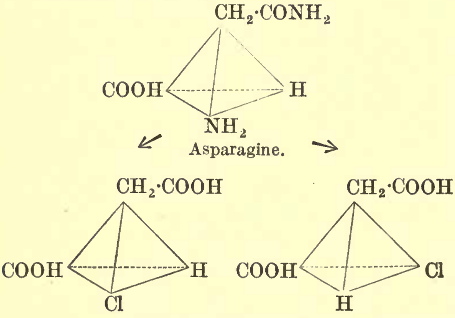
The 'Walden Inversion.' Pasteur showed that *d*-tartaric acid can be converted into *l*-tartaric acid by an indirect process. By heating *d*-tartaric acid under certain circumstances (Pasteur, Compt. rend. 1853, 37, 162; Jungfleisch, Bull. Soc. chim. 1872, 18, 201; Winther, Zeitsch. physikal. Chem. 1906, 56, 466, 720), a rearrangement of the groups about the asymmetric atoms takes place and ultimately an inactive mixture of racemic acid and *meso*tartaric acid is obtained. The racemic acid can then be resolved by one or other of the processes he had discovered. It would be possible, theoretically, to transform practically the whole of a given quantity of *d*-tartaric acid into the lævo variety, but the experimental difficulties would be very great. Since the method proceeds by racemisation, the substance operated on passes through a stage of inactivity.

In certain cases, however, it is possible to transform a molecule of one asymmetry into a molecule of opposite asymmetry without passing through any stage of inactivity. *Lævo*rotatory asparagine when acted on by nitrous acid yields *lævo*rotatory malic acid, and Walden found that *l*-malic acid yielded with phosphorus pentachloride, a *dextro*rotatory chlorosuccinic acid, which therefore might be supposed to correspond in configuration to *l*-malic acid and to asparagine. Tilden and Marshall, however (Chem. Soc. Trans. 1895, 67, 494), observed that *lævo*rotatory asparagine gave with nitrosyl chloride a *lævo*rotatory chlorosuccinic acid; whilst Walden, about the same time, discovered (Ber. 1895, 28, 2769) that this asparagine treated directly with bromine and nitric oxide gave a *lævo*rotatory bromosuccinic acid. Thus, starting from *lævo*rotatory asparagine, we can prepare according to the reagents used, either *lævo*rotatory or *dextro*rotatory chlorosuccinic acid.

Later, Walden (Ber. 1896, 29, 133) completed the following cycle :—

$$\begin{tikzcd}
l\text{-Malic acid.} \arrow[r, shift left, "PCl_5"] & d\text{-Chlorosuccinic acid.} \arrow[l, shift left, "KOH"] \arrow[d, "Ag_2O"] \\
l\text{-Chlorosuccinic acid.} \arrow[u, "Ag_2O"] \arrow[r, shift left, "KOH"] & d\text{-Malic acid.} \arrow[l, shift left, "PCl_5"]
\end{tikzcd}$$

Caustic potash and silver oxide act thus on the chlorosuccinic acids in an exactly opposite manner. One of these changes must be abnormal being accompanied by an exchange of two of the radicles attached to the asymmetric carbon atom. In one case the NH$_2$ group of the asparagine is replaced directly; in the other it, or the chlorine atom which is substituted for it, exchanges places at the same time with one of the other groups.



Chlorosuccinic acid.

These reactions are generally accompanied by a little, and often by a great deal, of racemisation.

So far, little of a really general character has been discovered about this most interesting reaction. For further details the papers of Walden (Ber. 1899, 32, 1833), Fischer (*ibid.* 1907, 40, 489; 1908, 41, 889, 1286, 2891; Annalen, 1911, 381, 123), and McKenzie (Chem. Soc. Trans. 1908, 93, 811; 1910, 97, 2564, etc.) should be consulted in addition to those already mentioned. *See* also the Chemical Society's Annual Reports, and P. F. Frankland, Chem. Soc. Trans. 1912, 101, 672.

II. APPARATUS.

The apparatus used by Biot (Ann. Chim. Phys. 1840, [ii.] 74, 428) and others consisted of a polarising mirror, the light from which, after passing through the substance under investigation, was examined by means of a double refracting rhomb of Iceland spar, or a prism such as that of Rochon or Wollaston, adjustment being made to those positions in which one or other of the images vanished.

A great improvement was made by Nicol (Edin. New Phil. Jour. 1828, [ii.] 6, 83; 1831, [ii.] 14, 372; 1839, [ii.] 27, 332), who invented the prism bearing his name (Fig. 9). It is usually made from a rhomb of Iceland spar about three times as long as broad, and the end faces, ABCD and EFGH should first be ground down so as to reduce the acute angles EAC and CGE from 71° to 68°, but this seems seldom to be done (S. P. Thompson, Phil. Mag. 1886, [v.] 21, 479). The prism is then cut through in the plane EKCL perpendicular to the principal section, in this case the plane through ACGE. The plane EKCL[1] makes an angle of 90° with the faces ABCD and EFGH. The two halves of the prism are then cemented together again in their original position by means of Canada balsam or Copaiva balsam, the indices of refraction of which lie between those for the ordinary and the extraordinary rays. The index of refraction of the ordinary ray being 1·654 and that of Canada balsam 1·55, it can easily be shown that any ray whose angle of incidence is greater than 69·5°, will be reflected out of the prism. On looking through the prism and tilting it so as to allow the rays to fall very obliquely on the face ABCD, this limit is marked by a series of interference spectra.

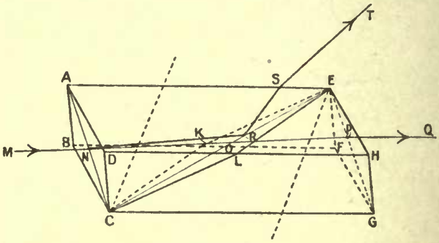


FIG. 9.

The other limit is conditioned by the fact that whereas the index of refraction of the ordinary ray, 1·654, applies in any direction through the crystal, that for the extraordinary ray, 1·483, only holds perpendicular to the optic axis. As the direction of the ray through the crystal approaches more nearly to that of the optic axis, the value of μ_e approaches 1·654, and in some intermediate position will have the value 1·55, equal to that of the Canada balsam. All extraordinary rays having a value greater than this are liable, like the ordinary rays, to be totally reflected at the balsam film. Fig. 10 shows the prism in section through ACGE. All rays below WV—such that the angle VXC is about 10°—ordinary or extraordinary, suffer total reflection.

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[1] It should be noted that the direction of the plane of section is practically immaterial; all that is necessary is that it should make a suitable angle with the rays traversing the prism. If the plane were laid from D to F the ordinary rays, the vibrations of which are perpendicular to this plane, would be reflected out to the remote side of the prism, whilst the extraordinary rays would pass on as before.

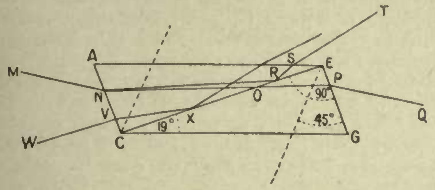

FIG. 10.

On tilting the prism so that the rays fall almost normally on the refracting face, this limit is marked by a broad blue and violet band. All rays, therefore, between MN and WV should be polarised in passing through the prism. The angle between these directions is some 32°.

The action of the prism does not depend on the *separation* of the two rays which occurs in the crystal. It is usually a cone of light that enters the prism so that ordinary and extraordinary rays may travel side by side, but on account of their different velocities in the crystal the former are totally reflected at the film whilst the latter pass through it. The vibrations constituting the ordinary ray are supposed to take place in a plane parallel to BD, those of the extraordinary ray in one parallel to AC, and therefore they are polarised in planes at right angles to these.

Fig. 11 represents a Nicol prism, end on. The principal plane passes through AC perpendicular to the plane of the paper. If a source of light be examined through two Nicols placed one behind the other so that their principal planes coincide (Fig. 12), the vibrations which pass through EFGH—the remote prism, the polariser—and which are parallel to EG, will also pass through ABCD; but when the prisms are crossed (Fig. 13), the light which passes through EFGH, vibrating parallel to EG, is stopped by the analyser, ABCD, so that part of the field appears dark.

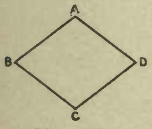

FIG. 11.

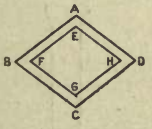

FIG. 12.

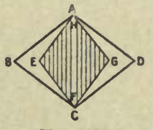

FIG. 13.

The Nicol prism, however, has several defects, one being the expense of large, clear pieces of spar. For this reason, Foucault (Compt. rend. 1857, 45, 238) invented a prism (Fig. 14) whose length is only about 1·25 times that of one of the sides of the refracting face, the plane of section making with the upper and lower edge an angle of 59°. The Canada balsam is replaced by air. An ordinary ray in the prism incident on this film at any angle greater than 37° 10′ will be totally reflected, the field being limited on this side by interference fringes; an extraordinary ray incident on the film at any angle greater than 42° 20′ will also be totally reflected, the limiting position being marked by a broad red band. Between these angles ordinary rays will be totally reflected and extraordinary rays will pass through. The field of view is thus very narrow, only comprising for the rays before they enter the prism, some 8°.

Again (1), part of the light incident on the sloping end face of a Nicol is reflected there, and (2) a ray of light falling on the prism in the direction of the axis of length, emerges parallel to its original direction but somewhat displaced, so that if the Nicol is rotated the image circles round the field, this being the case even if the ends of the prism are cut square, as shown in Fig. 15. The extraordinary ray will pass through the prism without displacement only if the refracting surface is cut parallel to the optic axis. A prism, cut as shown in Fig. 16, which partly corrects these faults, was first described by Hartnack and Prazmowski (Ann. Chim. Phys. 1866, [iv.] 7, 181). The end faces are still inclined at an angle to the axis, but the plane of section is perpendicular to the optic axis.

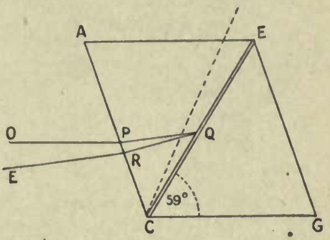

FIG. 14.

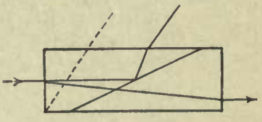

FIG. 15.

S. P. Thompson (Phil. Mag. 1886, [v.] 21, 478) modifies the Nicol prism so as to improve considerably its polarising properties. LIZP (Fig. 17) represents a section of a rhomb of spar, LJ being the direction of the optic axis. In an ordinary Nicol, the plane of section would pass from L to Z. The acute solid angles at I and P are cut off by the parallel planes LA, ZB, such that ILA=40°; the plane of section AB is almost at right angles to LA and BZ. There is thus comparatively little loss of material, and since the rays travel through the prism nearly perpendicular to the optic axis, the blue band which marks the limit of the transmitted extraordinary waves is thrown back so that with a shorter prism a field of about 39° is obtained.

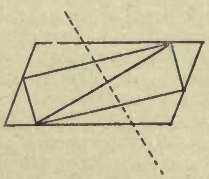

FIG. 16.

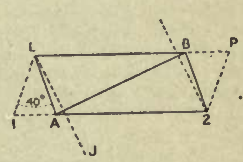

FIG. 17.

Other prisms, more or less alike, have been described by S. P. Thompson (Phil. Mag. 1881, [v.] 12, 349), R. T. Glazebrook (*ibid.* 1883, [v.]

15, 352), and P. Glan (Carl. Rep. 1880, 16, ii. 9, 570; Fortschr. d. Physik. 1880, [v.] 10, 247). Fig. 18 gives a rough idea of how this prism is situated relative to the original crystal. By planes perpendicular to the optic axis, the solid angles at C and E are first removed, the prism TVJP,WXYZ, being then cut out of the remaining spar. The plane of section is laid through TVZY. The optic axis is thus parallel to the refracting faces, TVJP and WXYZ, while the balsam film lies in a principal plane of section, that is, is parallel to the optic axis. There is great waste of material in cutting this prism, but its angle of view is increased and the polarisation is very perfect.

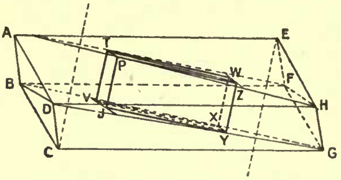

Fig. 18.

The prism (Fig. 19), described by Lippich (Wien. Sitzungsber. 1885, ii. 91, 1079; Beibl. Ann. d. Phys. 1887, 11, 455) for his polarimeter, has straight end faces of square section and a linseed oil film. The optic axis is perpendicular to the axis of length, but its position relative to the plane of section is immaterial.

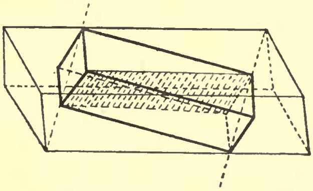

Fig. 19.

Fig. 20 shows the modern form of Nicol prism. A ray of light falling normally on the refracting face does not separate into two rays pursuing distinct paths through the crystal, but at the balsam film the ordinary ray is reflected out whilst the extraordinary ray passes on without deviation. If the optic axis is parallel to the plane of section the prism is of the Glan-Thompson variety, whilst if it is perpendicular to the plane of section the prism is technically referred to as a Lippich Nicol, although this is not strictly in accordance with Lippich's own statement (*v. supra*). The two parts of the prism are usually cemented together with linseed oil, which is superior to Canada balsam, but takes a long time to dry.

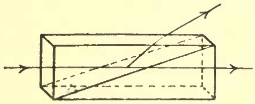

Fig. 20.

A paper read by E. Sang before the Royal Society of Edinburgh in 1837, discussing the theory of the Nicol prism, is remarkable, partly because fifty-four years elapsed before it was published (Proc. Roy. Soc. Edin. 1891, 81, 323), but also because it contained the first suggestion for a different type of prism, one to transmit the ordinary and reflect out the extraordinary ray. A right prism of dense glass whose index of refraction is, preferably, just the same as that for the ordinary ray in Iceland spar, is cut through obliquely (Fig. 20 may be taken to illustrate this prism also) and a thin lamina of Iceland spar or sodium nitrate, cut parallel to the optic axis, is introduced between the two parts and brought into optical contact with the cut faces or joined to them by means of some cement with an index of 1·654 or higher. A beam of light passing from the glass to the spar separates into two rays. The ordinary ray, with the same index in the spar as in the glass, goes straight through. For the extraordinary ray, however, the index is much lower in the spar than in the glass and if the ray is incident on the layer of spar at an angle of 74° or more, will not penetrate it at all. This idea was discovered also by Jamin (Compt. rend. 1869, 68, 221; Pogg. Ann. 1869, 137, 174), and a description of a prism on this principle was given by E. Bertrand (Compt. rend. 1884, 99, 538), which, by means of a double plane of section had a field of view of 98°.[1]

The Polarimeter. Nicol's prism appears first to have been used in a polarimeter by Mitscherlich (Lehrbuch der Chemie, 4th ed. 1844, i. 361), whose instrument (Fig. 21) was fitted at one end with a Nicol prism beyond which a source of monochromatic light was placed. At the other end, another Nicol was fixed to a pointer which could be turned round over a graduated scale. The prisms were then set to the position of maximum darkness, which is the zero point of the instrument. If an active substance be interposed between the crossed Nicols the field will become more or less illuminated,

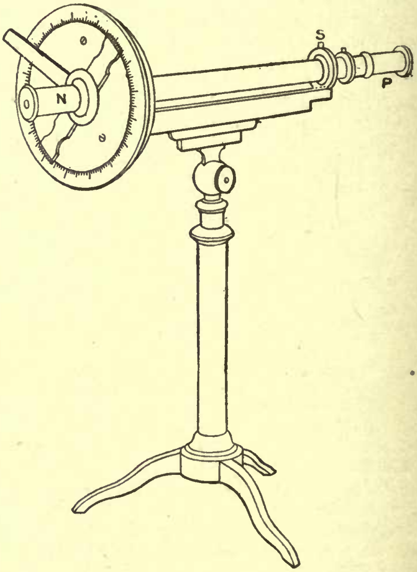

Fig. 21.

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[1] An article "On the Nicol Prism and its Modern Varieties," by S. P. Thompson, containing a bibliography of the subject, will be found in the Proceedings of the Optical Convention, 1905, p. 216.

and in order again to reach the position of maximum darkness the analyser must be turned round either towards the right hand—at the top of the scale, clockwise—or towards the left hand. In the former case, the substance is dextrorotatory, in the latter, lævorotatory. Adjustment is always made for the position of maximum darkness, since about this point a small displacement of the prism makes a considerable difference to the eye. The position of maximum brightness is much more difficult, in fact impossible, to adjust to.

Suggestions to obtain greater sensitiveness were made by Robiquet and by Wild, whilst a very ingenious prism was invented by Jellett (Brit. Assoc. Rep. 1860, 29, 13), but perhaps the most commonly adopted proposal was that of Laurent (Journ. de Physique, 1874, iii. 183; Dingl. poly. J. 1877, 223, 608). He placed between the polariser and the analyser, close to the former, a glass plate to which is cemented a half disc of quartz or gypsum cut parallel to the axis, called a half wave length plate. The general arrangement is shown in Fig. 22. P is the polariser, generally a Foucault prism, D the glass plate partly covered by the quartz half disc, N the analyser, usually a Nicol prism. The telescope OH is focussed on the straight edge of the quartz plate. In Fig. 23, let the circle FGKH represent the polariser diaphragm; FGK is the half disc of quartz whose optic axis may lie in any direction in the plane of the paper such as OB or DC or OG. Suppose that it is parallel to OC. The direction of vibration of light waves from the polariser, RSTU, passing through the diaphragm as seen end on, will be, for example, OA representing those falling on the glass plate, and DC, representing those falling on the quartz. The wave OA on its passage through the glass plate, may be regarded as resolved into two components, vibrating respectively parallel to OE and to OC. They travel with the same velocity and the same wave length, the resultant being thus always parallel to OA. A wave falling on the quartz plate, however, like DC, is resolved into a component parallel to DO, the ordinary ray, and one parallel to OC, the extraordinary ray, these being in reality very narrow ellipses (P. G. Tait, Light, 1889, p. 253; W. Voigt, Ann. d. Physik. 1905, [iv.] 18, 645). At the moment when the light touches the plate the particle of ether at D of the component DO is displaced towards O, and simultaneously the particle of ether at D of the component DB is displaced towards B, the resultant being in the direction DC. These travel through the plate with different velocities, that of the ordinary ray, DO, being the greater in the ratio 1·553/1·544. After a certain short interval of time, therefore, the extraordinary ray will have fallen one half wave length behind the ordinary ray. At this moment the vertical displacement is OC whilst the horizontal displacement is OD. The resultant is thus OB, the plane of vibration of the light having been turned through an angle $2a$ where a is the angle between the principal plane of the polariser and the optical axis of the quartz plate. As the two components proceed further into the quartz plate, the ordinary ray gains a whole wave length which brings the resultant back into its original position parallel to DC. In pursuing its way through the quartz plate, the plane of vibration of the light thus oscillates between the directions DC and OB. The plate is made of such a thickness that, on emergence, the ordinary ray is one half wave length ahead of the extraordinary ray for the kind of light used, and therefore the plane of vibration is parallel to OB. Whatever angle the original vibrations may make with OF, passage through the quartz plate inverts it symmetrically. The special character of this rotation of the plane of vibration of the incident light by the quartz plate should be carefully noticed. It is of an entirely different character from the rotation which would be produced by a plate of quartz cut perpendicular to the axis.[1]

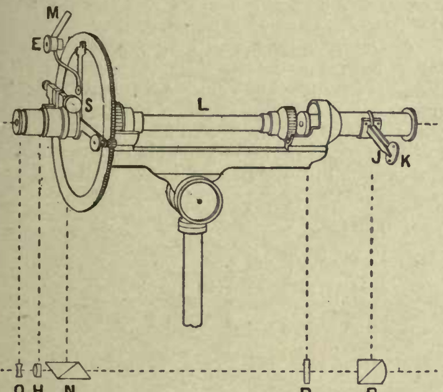

FIG. 22.

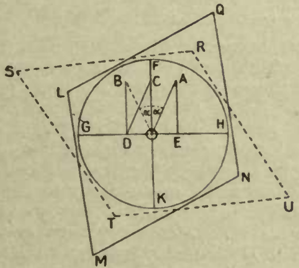

FIG. 23.

If now the light which has passed through the whole polariser system be examined by a Nicol prism, LMNQ, placed as shown in the figure, its principal plane at right angles to that of the polariser, the rays that have traversed the glass plate and vibrate parallel to AO will be stopped by the analyser and the half FHK of the circular field will appear dark. But those that have come through the quartz plate and are parallel to BO will pass to a considerable extent through the Nicol so that FGK will appear relatively bright. If the principal plane, LN, of the analyser be set perpendicular to BO, FGK will appear dark and FHK bright. Midway between these positions, the whole field should appear uniformly dark. If the analyser be turned through 90° so that its principal plane is parallel to the axis of the quartz plate the whole field should appear uniformly bright.

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[1] An instrument dependent on the action of a quartz plate cut perpendicular to the axis, or on a cell containing sugar solution, was suggested by J. H. Poynting (Phil. Mag. 1880, [v.] 10, 18).

The accuracy of a setting depends on the size of the angle α. If it be small a very slight movement of the analyser should suffice sharply to reverse the relative brightness of the sides of the field. The milled head is then oscillated back and forward from a position of darkness on one side to a position of similar darkness, as judged by the eye, on the other, the oscillations being gradually narrowed down until the median position is reached. The angle α must not be made too small, however, as then the amount of light cut off is very great and the eye ceases to be able to distinguish clearly between the brightness and darkness of the two halves of the field. The Laurent polarimeter can be used, of course, with only one kind of monochromatic light, being generally made for sodium light, which is purified by passage through a plate of potassium dichromate before entering the polarising system.

The Lippich polarising system is that most commonly used at the present time (Wien. Sitzungsber. 1885, ii. 91, 1079; 1895, ii. 105, 317). It is accurate, may be used with any kind of monochromatic light, and can be made to give a double or a triple field, the latter being the more delicate. Fig. 24 shows a plan of the arrangement. P is the polariser, just beyond which and taking the place of the quartz plate of the Laurent instrument, are two small prisms, each of the same depth but about one half the width of the polariser. For the small prisms both Hilger and Schmidt and Haensch use Lippich Nicols, whilst for the polariser Hilger uses a Lippich and Schmidt and Haensch a Glan-Thompson Nicol. Figs. 25 and 26 represent these systems in perspective, one of the small prisms being omitted in each case. The direction of the optic axis is indicated by the dotted arrows. The polariser is rectangular, but the small prisms have an angle of about 93° at D and E and are of about 87° at L and M (Fig. 24). The small prisms are fixed so that their faces LD and ME are inclined at a slight angle to the axis of the instrument, but the edges D and E are parallel or very nearly so. The eyepiece is focussed on these edges, which usually appear as faint lines dividing the field into three parts. Of these, F is illuminated by light which has passed through P and B; G by light which has passed through P only; and H by light which has passed through P and C. The polariser P is capable of rotation some 15° about the axis of the instrument, and in average work is placed so that its principal plane makes an angle of 4° to 5° with the principal planes of the small prisms. If now this system be viewed through the analyser with its principal plane placed perpendicularly to that of P, G should appear dark and F and H fairly bright. If the analyser be turned so that its principal plane is perpendicular to those of B and C, F and H should appear dark and G relatively bright. The analyser should then be oscillated about between these positions, the movements becoming smaller and smaller, until the final adjustment is reached.

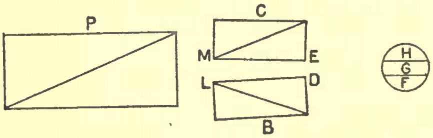

FIG. 24.

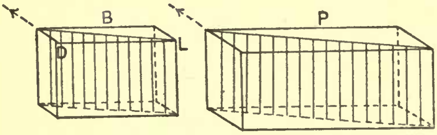

FIG. 25.

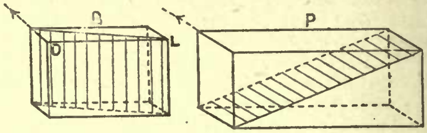

FIG. 26.

Source of light. The light commonly used for polarimetric purposes is that afforded by incandescent sodium chloride vapour. Fig. 27 represents one lamp suitable for producing it and another is shown in Fig. 28. In the former, salt is placed in a little movable spoon which is then swung into the flame; in the latter, a large size Méker burner is fitted with side pieces, in each of which are slits to receive two fairly stout platinum wires bent at right angles at the ends. Round each wire is rolled a piece of platinum gauze about 1″ × 1½″. Pieces of sodium chloride, which have been fused, are laid on the rolls of gauze after the burner has been lit. The salt melts and sinks into the meshes of the rolls, from which it slowly volatilises. The late Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 617) allowed what was practically an oxy-hydrogen flame to play on the side of a platinum boat containing sodium chloride. Another device has been described by H. E. Armstrong (Proc. Roy. Soc. 1908, A, 81, 113). Sodium bromide may be used instead of the chloride, as it gives a more intense light, but a serious disadvantage lies in the fact that the

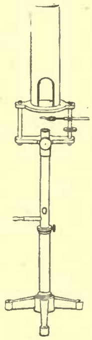

FIG. 27.

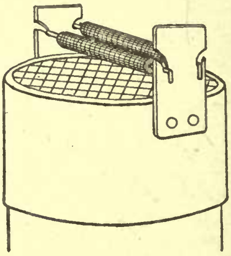

FIG. 28.

bromine vapour given off may injure the polarimeter.

The light from a burner volatilising sodium chloride is not truly monochromatic. There is a slight continuous spectrum, the blue from the Bunsen flame being fairly strong, so the light is usually filtered through a saturated solution of potassium dichromate, which removes the blue and green rays and is sufficient for most purposes. Sometimes a small cell, 1·5 cm. long containing uranous sulphate solution, may be used in addition to the potassium dichromate, as it removes any red rays that may be present; but the best method of purifying the light is by spectral analysis, a direct vision spectroscope being placed between the eye and the analyser or in front of the polariser. Details of the former method are given in a paper by Sir W. H. Perkin (Chem. Soc. Trans. 1906, 89, 609).

In a stricter sense, however, sodium light is not monochromatic, for its spectrum consists of two lines very close together, D_1 of $\lambda=589{\cdot}62$ $\mu\mu$ and D_2 of $\lambda=589{\cdot}02$ $\mu\mu$, so that the light reaching the polariser is a resultant whose optical centre' lies between these wave lengths in proportion to the relative intensity of the lines, which varies with the density of the vapour in the flame and this might have to be taken account of in very accurate work. It is therefore desirable to keep the brightness of the flame as constant as possible whilst a set of readings is being made. Otherwise as the brightness falls off the readings may vary a little.

Monochromatic light may also be obtained from the mercury arc lamp, in the spectrum of which there are four chief lines, one in the blue of 435·9 $\mu\mu$, two in the yellow of 579 and 576·9 $\mu\mu$ respectively, whilst the strongest and most important is that in the yellow-green of 546·1 $\mu\mu$. The other rays are filtered out by a suitable screen or by some method of spectral purification, and the last line is found very useful for polarimetric purposes (see Lowry, Phil. Mag. 1909, [vi.] 18, 320). If this light be utilised, however, comparative measurements with sodium light should always be given, as otherwise much of the value either of the new data or of the data already amassed for sodium light would be lost.

The polarimeter. Fig. 29 shows diagrammatically a modern polarimeter, as made by Schmidt and Haensch, Berlin, who, however, supply a different heating apparatus. The lamp A is so placed that a sharp image of the flame, or the diaphragm T in front of it, is thrown by the lens S on the diaphragm at M. B is a cell containing saturated potassium dichromate solution. By means of C, the polarising prism D can be turned about its axis of length, and thereby the angle altered which its principal plane makes with the principal planes of the small prisms at E. The heavy support F can be moved along the bed-plate O and clamped in any desired position. The observation tube K lies in a wider tube which passes through a copper bath HHHH containing water or other liquid. This bath is kept at any desired temperature by means of the thermo-regulator V (J. Soc. Chem. Ind. 1902, 21, 456) and the stirrer W. A thermometer U indicates the temperature inside the tube LG, which may be taken as identical with that in the observation tube. LG is closed at L and G by two wooden blocks, the holes in which are closed by small glass discs. Q, the analysing Nicol, is fastened to the graduated circle P, which is enclosed in a cover to protect it from the fumes of the laboratory. The lever X attached to the analyser and the graduated circle, makes the rough adjustment; the fine adjustment is made by means of the screw R. There is also another screw (not shown in the figure) by which the analyser can be turned about its axis independently of the graduated circle to adjust the zero point of the instrument. It may be noticed that when the half shadow—the sensitiveness—is altered by moving the lever C, the zero point is thereby also altered. The sensitiveness ought therefore only to be varied very cautiously and the zero point should be ascertained at frequent intervals, best along with each observation. For an interesting case

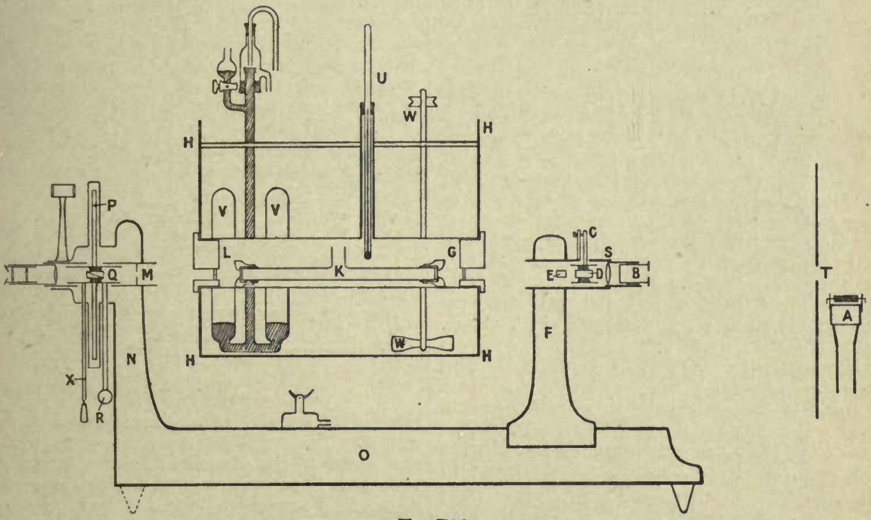

Fig. 29.

in point, see Chem. Soc. Trans. 1905, 87, 618.

The water in the thermostat HHHH should be covered with a layer of medium paraffin oil, which, by preventing evaporation, tends to keep the temperature constant. By means of the apparatus shown, the bath can be kept within about 0·01° of a given temperature for several months.

For experiments at temperatures above 80°, a rather small bath filled with oil is best—when the temperature can be raised to 170° or still higher if the joints of the bath are brazed.

Another form of heating apparatus is shown in Fig. 30. P is the polariser and A the analyser of the instrument. Between these, and having the same axis, is supported in some suitable manner, a double cylinder of brass or copper. The observation tube rests in the position shown, and the tubes E and D allow either of a current of water at some definite temperature being circulated through the cylinder or of steam or other vapour such as that of aniline or nitrobenzene being blown through the apparatus until the temperature has become constant in the observation tube. For an illustration of an instrument fitted in just a slightly different manner, see Scheuer, Zeitsch. physikal. Chem. 1910, 72, 569.

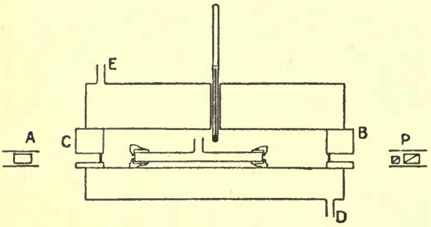

FIG. 30.

Polarimeter tubes. Fig. 31 shows the end of a polarimeter tube of the simplest type. Near each end of the glass tube there is fastened a metal collar having a screw cut on it. The ends of the tube are ground parallel and fitted with discs, A, of glass, which ought always to be carefully examined before use as occasionally they are slightly active on account of internal strain, when they should, of course, be rejected. Metal caps press the glass discs against the ends of the tube, rubber washers equalizing the pressure between them. The caps must not be screwed on too tightly as this may cause the discs to become birefringent and vitiate the readings. In some patterns of tube, a bayonet joint is used instead of a screw so that the pressure on the discs is at least always the same.

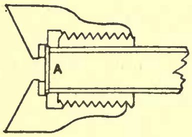

FIG. 31.

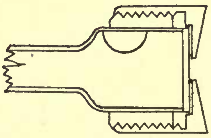

FIG. 32.

In some tubes one end is of the form shown in Fig. 32. Any bubble that has developed owing to contraction on cooling, can easily be moved into the expanded part of the tube where it does not interfere with the field of view. Especially in small tubes, however, the expanded end greatly increases the capacity of the tube, which is often a serious objection, and tubes of the form shown at K in Fig. 29 are much to be preferred, as they readily allow for any contraction or expansion, and can therefore be used for determinations over a moderate range of temperature if care be taken not to melt the sealing wax securing the collars on to which the caps are screwed. Jacketted tubes are also used such that water or other liquid at a desired temperature can be circulated round the tube. This involves the supply of water at constant temperature, which is rather troublesome; a suitable form of apparatus for this is described by Lowry (Trans. Faraday Soc. 1907, 3, 119). With many polarimeters, on account of the form of the stand, this is the only method of heating that can be adopted; but, wherever possible, it is better to use a thermostat like that shown in Fig. 29, which can be adjusted to any required temperature. In sugar factories, for instance, where, especially in the case of invert sugars, it is desirable always to polarise at a definite temperature to avoid the necessity of correcting the readings, a thermostat might be kept at one temperature for, probably, a year at a time without the necessity of renewing any of the parts, and would be found very useful.

Tubes like that shown in Fig. 33, are suitable for investigations over a wide range of temperature. A glass tube with a side piece is fitted, somewhat loosely, at each end with a brass ring K. The discs are then placed in position and short pieces of rubber tubing drawn over the ends of the tube so as to project beyond the discs, thus serving to prevent leakage and as washers as well. Two other brass rings, M, L, are placed, one at each end and secured there by brass rods which pass freely through three holes in M and K, K, and screw into holes in L. The rings K, K should be near the ends of the tube, their object being to keep it in position between the rings M and L. This tube may be used up to a temperature of about 180°, at which the rubber becomes very soft. For slightly different forms, see Chem. Soc. Trans. 1901, 79, 170.

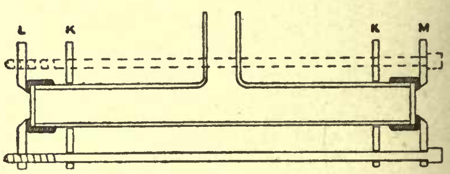

FIG. 33.

Determination of density. Another operation of importance in polarimetric work is the determination of the specific gravity of liquids. This may be done by means of a hydrostatic balance, by hydrometers, by the Westphal balance, by specific gravity bottle, by dilatometer or by pyknometer. The last is probably the most accurate as well as the simplest and is most generally used. For details see article SPECIFIC GRAVITY.

Methods of expressing rotatory power. Several expressions are in use for indicating the rotatory power of an active compound.

The *observed rotation* is the angle through which the plane of polarisation is turned by a layer of the liquid substance, one decimeter in thickness. Thus $\alpha^{20}_D + 34{\cdot}51°$ means that the angle α, through which the yellow light from a sodium flame would be turned to the right—the observer looking *against* the direction of the ray—at 20°, after passing through unit length of the substance, is 34·51°.[1] If the magnitude of the rotatory power be used merely to indicate the purity of the compound, or for analytical purposes, this expression is as useful as any; but for the comparison of the rotations shown by a given substance under different conditions—of temperature, for instance—it would not be satisfactory, and since Biot's early experiments seemed to show that change of temperature only affected rotation in proportion to the expansion produced, and also that the rotation of a dissolved substance was proportional to its concentration, he introduced the idea of *specific rotation*, which he supposed to be an invariable constant not dependent on the condition of the substance (Mém. de l'Acad. 1835, 13, 116; Ann. Chim. Phys. 1844, [iii.] 10, 18). The specific rotation is indicated by the symbol $[\alpha]$, and for a homogeneous liquid $[\alpha]^t_D = \frac{\alpha^t_D}{d}$, where α is the observed rotation for the D line at the temperature $t°$, and d is the density of the substance at $t°$ as compared with water at 4°, as unity.

In the case of a dissolved active compound the strength of the solution must be taken account of, and may be expressed in several ways, the two commonest being as concentration and as percentage composition. Concentration, c, indicates grams of substance per 100 c.c. of solution, the substance being weighed into a graduated flask which is then filled up to some definite volume with the solvent. Then $[\alpha]^t_D = \frac{\alpha^t_D}{c}$. This method, however, is open to the objection that the concentration may, and usually does, vary with change of temperature. In the second case, both active substance and solvent are weighed. The percentage composition, p, is then the weight of substance in 100 grms. of the mixture, and is, of course, independent of the temperature. In this case, $[\alpha]^t_D = \frac{\alpha^t_D}{p \times d}$.

According to Biot, the specific rotation is 'the angle of rotation which a liquid would show if it contained in a volume of one cubic centimetre, one gram of active substance, and should act on the polarised ray through a column one decimetre in length,' but it is simpler to define it as the rotation which would be shown by 10 grms. of the homogeneous substance, or that quantity of solution which contains 10 grms. of it in a tube of 1 sq. cm. cross section, just long enough to contain it. The specific rotation, however, contrary to Biot's early expectations, is by no means necessarily constant, but may vary greatly with temperature, nature of the solvent and concentration.

It is scarcely to be expected that the rotations of different compounds can be compared simply for 10 grms. of each, so the molecular rotation is usually calculated in such cases $[M]^t_D = \frac{[\alpha]^t_D \times M}{100}$. It is the rotation produced by one-tenth of a gram molecular weight of a homogeneous substance, or that quantity of a solution which contains one-tenth of a gram molecular weight, in a tube of one square centimetre cross section just long enough to contain it. This supposes the rotation to be proportional to the whole weight of the molecule, and Guye has suggested that since one looks through the molecule it might perhaps be better to take the rotation as proportional to its diameter, and therefore he introduced the idea of molecular deviation, $[\delta]^t_D = \alpha^t_D \sqrt[3]{\frac{M}{d}}$, but so far it cannot be said that the regularities discovered by the use of this formula are any better than those derived from the molecular rotation, and as it involves greater trouble in calculation it has not been very much used (Compt. rend. 1893, 116, 1454).

III. Quantitative.

Rotation and chemical constitution. Although Biot, in his later work, discovered that the rotation of an active compound was a property much more sensitive to external conditions than he had originally imagined, little notice was taken of the fact, and, in consequence, many of the older data, in the collection of which considerations of temperature, solvent, concentration and even the light used, were ignored, are rendered practically useless. Within the last quarter of a century, however, these factors have received greater attention, and when, for want of a better plan, the rotation values are all taken at one definite temperature, a few regularities appear between the rotation data and the chemical constitution of homogeneous liquid substances.

It is perhaps natural to take first the changes which occur in passing from member to member of a homologous series.

Table I.—Rotation Values of the *l*-Malates.

	$[\alpha]^{20}_D$		$[M]^{20}_D$	
Malic acid[1]	+ 5·89°	12·74°	+7·89°	18·99°
Methyl malate[2]	− 6·85	3·33	−11·10	8·25
Ethyl malate[2]	−10·18	1·44	−19·35	5·97
n-Propyl malate[2]	−11·62	−0·09	−25·32	1·06
n-Butyl malate[3]	−10·72	−0·08	−26·38	0·81
Amyl malate[2]	− 9·92	−3·00	−27·19	−2·42
Capryl malate[2]	− 6·92		−24·77	

Table II.—Rotation Values of the Tartrates.

	$[\alpha]^{20}_D$		$[M]^{20}_D$
Tartaric acid[4] .	−0·30°	2·37°	−0·45°
Methyl tartrate[5] .	+2·07	5·67	+3·68
Ethyl tartrate[5] .	+7·74	4·94	+15·95
n-Propyl tartrate[5] .	+12·68	−2·38	+29·66
n-Butyl tartrate[6] [19°]	+10·30		+26·99

[1] Extrapolated from data by Schneider (Annalen 1881, 217, 257) from aqueous solutions.

[2] Walden, Zeitsch. physikal. Chem. 1895, 17, 245.

[3] Anschutz and Reiter, *ibid.* 1895, 16, 419.

[4] From data by Thomsen, J. pr. Chem. 1885, [ii.] 32, 213.

[5] Patterson, Chem. Soc. Trans. 1904, 85, 765.

[6] Freundler, Bull. Soc. chim. 1894, [iii.] 11, 305.

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[1] Often the rotation observed in any tube is called the 'observed rotation,' the length of tube being specified.

TABLE III.—ROTATION OF VARIOUS ESTERS DERIVED FROM GLYCERIC ACID.[1]

	A Glycerate $[M]_D^{15}$	B Diacetyl-glycerate $[M]_D^{15}$	A – B	C Dimethoxy-propionate $[M]_D^{15}$	A – C
Methyl .	–5·76°	–24·56°	18·8°	–103·8°	98°
Ethyl .	–12·30	–35·56	23·26	–114·4	102·1
n-Propyl .	–19·15	–45·17	26·06	–122·5	103·3
sec-Propyl	–17·49	–41·69	24·20	—	—
n-Butyl .	–21·37	—	—	–124·2	102·8
*iso*Butyl .	–23·05	–50·38	27·33	—	—
n-Heptyl	–23·05	–47·89	24·84	–127·9	104·8
n-Octyl .	–22·28	–47·92	25·64	–125·6	103·3

TABLE IV.

	$[M]_D^{20}$
Menthyl formate	–146·3°
„ acetate	157·3
„ propionate	160·2
„ *n*-butyrate	157·1
„ *n*-valerate	157·3
„ *n*-caproate	157·7
„ *n*-heptylate	157·7
„ *n*-caprylate	155·8

TABLE V.—SECONDARY ALCOHOLS.

	$[M]_D^{20}$
sec-Propyl-methyl-carbinol	+4·3°
„ ethyl „	15·4
„ *n*-propyl „	24·7
„ *n*-butyl „	33·3
„ *n*-amyl „	32·9
„ *n*-hexyl „	33·9
„ *n*-octyl „	34·5
„ *n*-decyl „	34·5

(Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624).

With the above data several points may be illustrated.

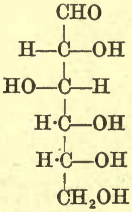
1. Although ordinary malic acid in aqueous solution is lævorotatory like the esters derived from it, and is called *l*-malic acid, it is to be inferred from the behaviour of its concentrated solutions that the substance, if it could exist at the ordinary temperature in the liquid form, would show a positive rotation. Solutions of above $p=34$ have a positive rotation at 20°.

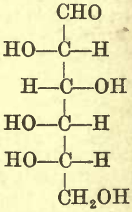
TABLE VI.—ROTATION OF ESTERS OF VARIOUS ACIDS[2] (temperature approximately 20°).

Ethyl	$[M]_D$	Ethyl	$[M]_D$	Ethyl	$[M]_D$	Ethyl	$[M]_D$
Lactate	–12·2°	Glycerate	–12·3°	Malate	–19·8°	Tartrate	+15·86°
Acetyl-lactate	–79·7	Diacetyl-glycerate	–35·6	Acetyl-malate	–52·3	Diacetyl-tartrate	+10·0
Benzoyl-lactate	+59·0†	Dibenzoyl-glycerate	+89·2	Benzoyl-malate	–11·4	Dibenzoyl-tartrate	–123·6
Methoxy-propionate	–118·9	Dimethoxy-propionate	–114·4	—	—	—	—
Methyl		**Methyl**		**Methyl**		**Methyl**	
Lactate	–8·6	Glycerate	–5·8	Malate	–11·1	Tartrate	+3·8
Methoxy-propionate	–112·7	Dimethoxy-propionate	–103·8	Methoxy-succinate	–92·4	Dimethoxy-succinate	+180·0†

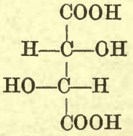
Tartaric acid, Table II., behaves similarly, but in an opposite sense, for although it itself and its salts in aqueous solution as well as its simple esters in the homogeneous state, have a positive rotation and it is called *d*-tartaric acid, it would nevertheless give, if it could exist in the liquid homogeneous condition, a negative rotation.

2. Although to the names of many compounds the letters *d*- and *l*- are prefixed merely to indicate the sign of their rotation, Emil Fischer has been able to trace a genetic relationship between many substances related to the sugars, and prefixes the letters *d*- and *l*- to the names of compounds according to the structural relationship which they bear to glucose. In a long series of researches, pre-eminent alike for manipulative skill and reasoning power, Fischer has shown that natural glucose must have one or other of the structural formulæ:


d-Glucose.


l-Glucose.

and as it is hardly probable that we shall ever be able finally to discriminate between these, he has made the above arbitrary selection. *d*-Tartaric acid must then be, as he has shown,


d-Tartaric acid.

the two upper asymmetric carbon atoms of the glucose molecule corresponding with the two asymmetric atoms of tartaric acid. For *d*-malic acid the formula is

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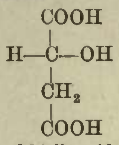
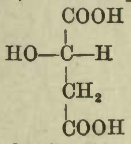
[1] For references see P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 865.

[2] From P. F. Frankland and Gebhard, Chem. Soc. Trans. 1905, 87, 867, which see regarding data marked thus †.



d-Malic acid.

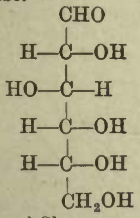
and the structure of its isomeride, ordinary natural *l*-malic acid, will be represented by



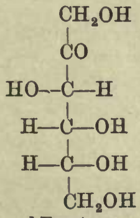
l-Malic acid.

(Ber. 1896, 29, 1377).

Thus, although for ethyl dibenzoyltartrate $[M]_D^{20} = -123{\cdot}6°$ (Table VI.), the substance is nevertheless a *d*-compound. Similarly, fructose with a high negative rotation is *d*-fructose on account of its structural relationship with *d*-glucose, the configuration about the three lowest asymmetric carbon atoms being the same in each case.



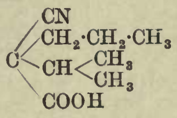
d-Glucose.



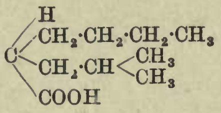
d-Fructose.

3. Table I. shows that the specific rotation of the malates becomes increasingly more negative as the series is ascended until the *n*-butyl ester is reached, and from this point the rotation rises again. There is thus a minimum (maximum negative) rotation at the *n*-propyl term. When the molecular rotation is considered, however, the behaviour is not the same, the lowest rotation occurring at the amyl term. With the tartrates, on the other hand, a maximum occurs both in the molecular, and the specific, rotation, at the same—the *n*-propyl—term. In the molecular deviation for these different esters the minimum might possibly be found at some other term. The example illustrates a kind of difficulty that often occurs; we have no criterion to decide which method of reducing the observations is the best, but the molecular rotation is probably to be preferred to the specific rotation.

This tendency to rise to a maximum and then fall again may be seen in all the data of Table III., and has been much discussed in connection with an idea put forward simultaneously by Crum Brown (Proc. Roy. Soc. Edin. 1890, 17, 181) and by P. A. Guye (Compt. rend. 1890, 110, 714; 1893, 116, 1378, 1415), who suggested that a relationship might be detected between the rotation of a compound and the masses of the four radicles attached to the asymmetric atom. Guye proposed, for calculating the 'Product of Asymmetry,' a formula of such a character that when two of the masses became equal the expression reduced to zero. The formula predicted also the occurrence of maximum rotations at definite members of certain series, and in some cases maxima were found at, or about, these terms. But for the most part it failed entirely; the rotation of a compound does not become zero merely because two of the groups attached to the asymmetric atom are equal in weight. Fischer and Flatau (Ber. 1909, 42, 2981) have shown that, for instance, the isomerism between *n*-propyl and *sec*-propyl is sufficient to render them different groups so far as an asymmetric carbon atom is concerned. Thus *n*-propyl-*sec*-propyl—cyanoacetic acid



was found to have a rotation $[\alpha]_D^{20} \doteq +11{\cdot}3°$ in toluene solution $p=10{\cdot}4$, and *n*-butyl-*iso*-butyl-acetic acid



had in the homogeneous state $[\alpha]_D^{22} = +5{\cdot}73°$ (Fischer, Holtzapfel and v. Gwinner, Ber. 1912, 45, 247), and *n*-propyl-*sec*-propyl carbinol has $[M]_D^{20} = +24{\cdot}7$ (Pickard and Kenyon, Chem. Soc. Trans. 1912, 101, 624, Table V.).

4. Tables I., III. and V. show that the molecular rotation alters most rapidly in passing through the lower members of a homologous series, a comparative constancy being reached in the higher representatives. These are examples of a regularity first pointed out by P. F. Frankland and MacGregor (Chem. Soc. Trans. 1896, 69, 121), namely, that when substitution takes place in a molecule at a point comparatively remote from the asymmetric atom it is attended with but little change in rotatory power. Tschugaeff gives the data of Table IV. to show that: 'In every series of homologous derivatives of any asymmetric substance there occurs, at least within certain limits, an inverse proportionality between the values of the specific rotation and the corresponding molecular weight' (Ber. 1898, 31, 366). To these may be added the data by Pickard and Kenyon in Table V. According to Frankland, the general behaviour, especially the existence of a somewhat indistinct and irregular maximum, may be explained thus: 'According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return upon itself, and, beyond this, further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to

an increase in the rotatory power' (Chem. Soc. Trans. 1899, 75, 368; 1912, 101, 658).

TABLE VII.—ROTATION OF SUBSTITUTED ETHYL TARTRATES.

(Ethyl tartrate, $[M]_D^{20} = +15{\cdot}86°$.)

Substituent	$[M]_D^{20}$	Substituent	$[M]_D^{20}$
Mono-acetyl .	+23·1°	Di-acetyl .	+9·9
„ monochloro-acetyl	32·3	„ monochloro-acetyl .	+25·5
„ trichloro-acetyl .	54·7	„ trichloro-acetyl .	+67·1 [1]
„ phenacetyl	98·5	„ phenacetyl	+79·2
„ benzoyl .	61·4	„ benzoyl .	−247·1
„ *o*-toluyl .	38·2	„ *o*-toluyl .	−266·5
„ *m*-toluyl .	44·0	„ *m*-toluyl .	−306·3
„ *p*-toluyl .	63·5	„ *p*-toluyl .	−484·4
„ nitro .	89·23 [2]	„ nitro .	+80·45 [2]
„ *m*-nitro-benzoyl	44·38 [3]	„ *m*-nitro-benzoyl .	−357·3 [4]

5. A regularity emerging from the data of Table VII. was first pointed out by McCrae and Patterson (Chem. Soc. Trans. 1900, 77, 1108). One acyl group, introduced into the molecule of ethyl tartrate, brings about in each case a considerable increase of rotation, whilst the introduction of a second (with the one exception of the trichloroacetyl derivatives) causes a diminution, which for the purely aromatic radicles, benzoyl and the toluyls, is very great indeed, the positive rotation of the mono-substitution product being changed into a very high negative rotation.

6. Another question that has attracted attention relates to the effect upon rotation of the presence of multiple bonds. It is often asserted that a double bond raises the rotation, but as the following figures show this general statement requires qualification.

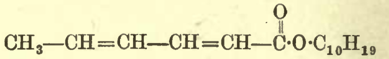
TABLE VIII.

Menthyl ester of	$[M]_D^{20}$ (Alcoholic solution $p=9$)
Butyric acid . .	−164·7°
Crotonic „ . .	203·1
$\Delta^{\alpha\beta}$-Pentenonic acid . .	177·1
$\Delta^{\beta\gamma}$ „ „ . .	172·5
$\Delta^{\gamma\delta}$ „ „ . .	160·2
$\Delta^{\alpha\beta}$-Hexenoic „ . .	172·4
$\Delta^{\beta\gamma}$ „ „ . .	164·1
$\Delta^{\gamma\delta}$ „ „ . .	153·5
$\Delta^{\delta\epsilon}$ „ „ . .	154·4
$\Delta^{\alpha\beta}$-Heptenoic „ . .	175·5

(Rupe, Annalen, 1903, 327, 166).

The double bond exerts a greater effect the nearer it is to the asymmetric centre. Menthyl butyrate has, almost exactly, what Tschugaeff calls the constant molecular rotation for the menthyl esters, but when a double bond is introduced into the molecule to give menthyl crotonate, the rotation is very markedly augmented, the same thing on a smaller scale being noticeable for the other unsaturated acids in which the double bond is in the $\alpha\beta$-position. As the double bond moves further from the asymmetric centre the rotation gradually reverts to the normal value, the behaviour being thus in accordance with the regularity of Frankland and MacGregor already alluded to under 4.

Rupe has also shown that the rotation of menthyl sorbate



$$\mathrm{CH_3{-}CH{=}CH{-}CH{=}CH{-}\overset{\overset{O}{\|}}{C}{\cdot}O{\cdot}C_{10}H_{19}}$$

$[\alpha]_D = -88{\cdot}53°$, is much higher than that of $\Delta^{\beta\gamma}$-hexenoic acid menthyl ester,

$$\mathrm{CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CO{\cdot}O{\cdot}C_{10}H_{19}},$$

$[\alpha]_D = -65{\cdot}11°$, which he attributes to the presence of a system of alternate single and double bonds, such as has been called by Thiele, conjugated, the menthyl sorbate containing a set of three conjugated double bonds.

No perfectly general rule regarding the influence of double bonds can be formulated, however; thus it has been shown by Frankland and O'Sullivan (Chem. Soc. Trans. 1911, 99, 2327) that, whereas the rotation of propyl menthoxyacetate is less than that of allyl menthoxyacetate at 20°, it is greater at a temperature of 100°, whilst at about 38° the rotations of the two substances are equal. The effect of multiple bonds has been examined in a number of cases by Hilditch (*ibid.* 1909, 95, 1581).

In regard to the relative influences upon rotatory power which a substituent exerts in the *ortho*, *meta*, and *para* positions respectively, it has generally been found that the *para* di-substitution product has the greatest rotation and the *ortho* the least, whilst the phenyl derivative usually comes in between the *ortho* and the *meta* compounds (P. F. Frankland, Chem. Soc. Trans. 1896, 69, 1538; 1912, 101, 666; Cohen and Dudley, *ibid.* 1910, 97, 1737).

Influence of change of temperature on rotation. The early experiments of Biot indicated that temperature played a quite unimportant part in conditioning the rotation of active bodies, but later investigations, chiefly by P. F. Frankland, have shown that, in reality, its influence is of the greatest consequence. Rotation may increase or diminish with change of temperature, or it may appear to remain almost unaffected, but it is probable that when examined over a sufficient range, the rotation of an active compound will show a maximum or a minimum value, or perhaps several such. An idea of the behaviour met with will be obtained from Figs. 34 and 35, the former of which represents the influence of temperature change upon the molecular rotation of a number of closely related substances.

Methyl tartrate (not represented in the figure) is practically inactive at 0°, and if cooled below this temperature its rotation becomes negative; it therefore furnishes an example of a compound whose rotation passes through the point of inactivity at some definite temperature for light of a particular wave length. The rotation of ethyl tartrate is higher than that of the methyl ester and the increase of rotation on heating is somewhat greater. The point of inactivity would be reached about −34°. Curves for the *n*-propyl, *sec*-propyl, *iso*-butyl, *iso*-amyl, *sec*-octyl and allyl esters are also shown. The curves are, in general, alike, but even for such closely similar substances, the institution of comparisons between the rotation values at any one given temperature cannot yield very satisfactory results. The rotation values for these esters at 20° would not be in the same sequence as at, say, 180°. At the former temperature, for instance, allyl tartrate has a higher rotation than has *iso*-amyl tartrate, whereas at the latter the reverse is the case. Other examples are obvious.

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[1] Patterson and Davidson, Chem. Soc. Trans. 1912, 101, 378.

[2] In 9 per cent. methyl alcoholic solution, Frankland, Heathcote and Hartle, *ibid.* 1903, 83, 154.

[3] In 2·38 ethyl alcoholic solution, Frankland, Heathcote and Green, *ibid.* 1903, 83, 168.

[4] Homogeneous; Frankland and Harger, *ibid.* 1904, 85, 1578.

Temperature Rotation Curves for Various Esters of Tartaric Acid.

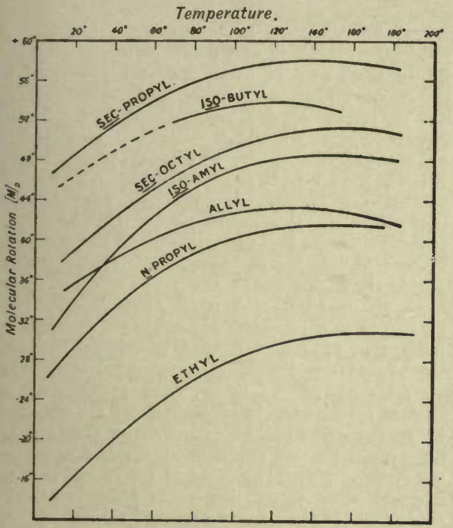


FIG. 34.

The curves of Fig. 35 refer to a number of compounds not so intimately related. The scale of the rotations is very much smaller, the curve for *sec*-propyl tartrate of Fig. 34 being included for comparison.

Temperature Rotation Curves for Various Esters.

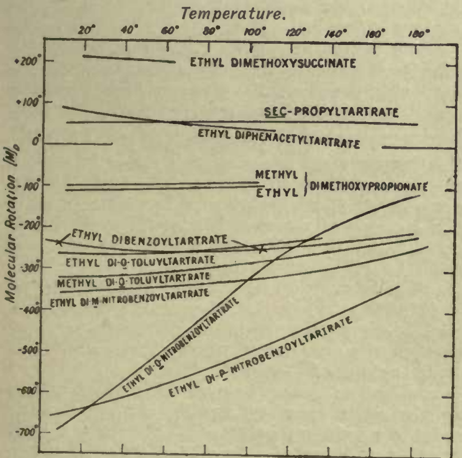


FIG. 35.

The uppermost curve represents the behaviour of ethyl dimethoxysuccinate, the rotation of which, $[M]_D^{20} = +210{\cdot}6°$, falls to 199·8° on heating to 60°. With this may be compared the curves for the methyl and ethyl esters of dimethoxypropionic acid, which have rotations at 20° of about −100°, becoming less negative as the temperature rises. These dimethoxypropionates are derived from *l*-glyceric acid which, in its configuration, corresponds to *l*-tartaric acid, so that the dimethoxypropionates, corresponding to *d*-tartaric acid, would have positive rotations of about +100°, gradually falling with rise of temperature, and would thus show a behaviour closely analogous to that of the dimethoxysuccinates, which with two asymmetric centres have a rotation almost twice as great. The other curves on the diagram represent data obtained by P. F. Frankland and his pupils, and exhibit the very great effect which change of temperature may exert. That for ethyl dibenzoyltartrate is of especial interest as it shows a minimum of −258° at a temperature of 63° (Frankland and Wharton, Chem. Soc. Trans. 1896, 69, 1587). It was the first recorded instance of this phenomenon, but a considerable number of other cases have since been found. All the curves in Fig. 34 show distinct maxima, and maxima also exist in the temperature-rotation curves for ammonium and sodium molybdanylbimalates (Grossmann and Pötter, Ber. 1904, 37, 84), for solutions of sodium and potassium tartrates, for some of the potassium alkyl tartrates (Patterson, Chem. Soc. Trans. 1904, 85, 1116) and for homogeneous menthol (Patterson and Taylor, *ibid.* 1905, 87, 33) and in other cases.

The remaining curves represent the results of observations by Frankland and Wharton (Chem. Soc. Trans. 1896, 69, 1309, 1583) and Frankland and Harger (*ibid.* 1904, 85, 1571). That for ethyl dibenzoyltartrate is much like the graph for ethyl di-*o*-toluyltartrate, whilst those for ethyl di-*m*-nitrobenzoyltartrate and ethyl di-*p*-nitrodibenzoyltartrate are again very similar. The behaviour of ethyl di-*o*-nitrobenzoyltartrate is most remarkable. The very high negative rotation diminishes with surprising rapidity as the temperature rises, and appears to have a point of inflection somewhere between 80° and 100°. The degree in which relationship between rotation and constitution depends on the temperature of comparison is strikingly apparent from this set of substances. At a low temperature, the *o*-nitrobenzoyl derivative has the greatest negative rotation, whilst at a temperature of 135° it would have the lowest, its graph cutting the other curves at intermediate temperatures. Nevertheless it is probably of the same type as the others. The rotation of ethyl dibenzoyltartrate is a minimum at 63°, and it seems likely that the di-*o*-toluyl derivative will reach a minimum value at a somewhat lower temperature, and similarly for the *m*-nitrobenzoyl derivative. The slope of the curve for ethyl di-*p*-nitrobenzoyltartrate is greater, and therefore its minimum should lie at a still lower temperature. Similarly, the last curve may also have a minimum of high numerical value at an even lower temperature. On the other hand, the di-*o*-nitrobenzoyl derivative may rise to a maximum, and it is probable that ethyl di-*p*-nitrobenzoyltartrate and the other esters also have maxima at successively higher temperatures. If this be true, the variation of the rotation of an active compound with change of temperature is a *periodic* phenomenon, and several maxima and minima might be expected to occur as one or other of the groups attached to the asymmetric atom preponderates. Unfortunately it is difficult to examine the variation over a wide range of temperature.

Attempts are often made to express mathematically the relationship between rotation and temperature, the parabolic equation

$$\alpha=a+bt+ct^2,$$

being usually applied. If the above be true, however, this form cannot be the correct one to use; if it were, the rotation would not be a periodic function, but should proceed towards infinity both at low and at high temperatures, and the two limbs of the curve ought to be of exactly the same shape. Winther (Zeitsch. physikal. Chem. 1902, 41, 176) has calculated such an equation for ethyl tartrate and reduced it to the form

$$[\alpha]_D^t=14{\cdot}126-0{\cdot}000401[t-149]^2,$$

the temperature 149° being that of the maximum rotation. He suggested that the value of the specific rotation should be reckoned, not from zero, but from this maximum value, such a datum to be called the 'rational specific rotation,' $[A]_D^t$.

$$[A]_D^t=a-[\alpha]_D^{t^\circ}=b[t-149]^2$$

(*l.c.* 207).

Winther assumes that the temperature at which the maximum occurs is the same at least for the three esters with which he deals, but this is not the case (Patterson, Chem. Soc. Trans. 1908, 93, 1844). The curves of Fig. 34 show maximum rotations at temperatures as below.

TABLE IX.

Ester	Temperature	Maximum $[M]_D$
Ethyl tartrate	175°	+30·9°
n-Propyl ,,	150	41·65
sec-Propyl ,,	144	58·03
iso-Butyl ,,	120	53·9
iso-Amyl ,,	151	48·72
Allyl ,,	130	43·24
sec-Octyl ,,	160	51·46

It may be, however, that the maximum rotations occur at 'corresponding' temperatures at which it would be legitimate to compare with one another the rotation values of different active compounds, or that comparison should be made at temperatures connected in some simple manner with those at which the maxima occur. A suggestion of this sort was made by Patterson (Chem. Soc. Trans. 1904, 85, 765), based on the fact that the rotations of methyl, ethyl, and *n*-propyl tartrate would respectively become zero at 0°, −34°, and −60°; these may be 'corresponding' temperatures, and, as a first approximation, the rotations, of methyl tartrate, of ethyl tartrate, and of *n*-propyl tartrate may be directly comparable at T°, (T−34°), and (T−60°) respectively. The ratio of the rotations of the esters thus obtained remained nearly constant over a fairly wide range of temperature.

It may be added that when turpentine was converted into vapour it still retained its optical power (Biot, Ann. Chim. Phys. 1819, [ii.] 10, 73), and the same thing has been observed for certain derivatives of amyl alcohol (Guye and do Amaral, Arch. sc. phys. Genève, 1895, [iii.] 33, 409, 513; Compt. rend. 1895, 120, 1345; Wied. Beibl. 1895, 19, 792, 894).

Influence of pressure on rotation. To determine the influence of pressure on rotation is very difficult, since the pressure applied to the liquid must also be applied to the end discs of the containing tube, when they too become double refracting and optically active. In the one investigation which has been carried out on the subject, L. H. Siertsema (Arch. Néerl. Sci. 1899, [ii.] 2, 29; 1900, [ii.] 3, 79) found it necessary to immerse the polarising and analysing prisms in the liquid to be examined and submit them as well as the liquid to the pressure. It was found, for instance, that the rotation, 12·4°, of a decimetre layer of a cane sugar solution $c=18{\cdot}7$, was only altered by about 0·31° per one hundred atmospheres increase of pressure. (These figures are calculated from the numbers in the tables given by Siertsema.)

Rotation in solution. The rotation of an active compound in solution in an inactive liquid is usually different, and often very greatly different, from its rotation in the homogeneous condition. The behaviour of ethyl tartrate on dilution with water illustrates this well. The rotation of the homogeneous ester, at 20° ($l=1$ decimeter), is 9·4°, and if the tube were extended to twice its original length, without alteration of the cross section, water being added to fill up the resulting space, the rotation of the 2 decimeter layer of solution, after thorough mixing, would be 20·4°, or more than twice as much as before. If the tube were again doubled in length and more water added, the rotation would become 27·6°, and on continuing the process until the tube could be considered infinitely long, a rotation of 32·3° would ultimately be reached.

The curves shown in Fig. 36 represent the effect of several solvents of very different character, not upon the observed, but upon the specific rotation of this ester, at 20°. For pure homogeneous ethyl tartrate $[\alpha]_D^{20}=+7{\cdot}8°$, and this increases on mixture with water in such a manner as to reach the value +26·84° in an extremely dilute solution. In nitrobenzene, the increase of rotation is something the same as in water but the curve is different in shape and the effect of the solvent is greater, the rotation in very dilute solution being raised to +41°. In ethyl alcohol, the rotation diminishes slightly to reach a minimum value at a concentration of $p=60$, after which it increases to a final value of +9·13°. The behaviour of benzaldoxime is very remarkable: the rotation of the ester increases until $p=70$, at which point a maximum value of +13·6° is reached. Further addition of oxime then diminishes the rotation, so that at $p=22$ the solution becomes inactive, and at infinite dilution the specific rotation would be approximately −16°. The rotation therefore varies 30° between the extreme limits, and by about equal amounts on either side of zero (Chem. Soc. Trans. 1907, 91, 508). In acetylene tetrabromide the rotation of the dissolved ethyl tartrate diminishes very rapidly with diminution of concentration, the rate becoming greater as the dilution increases, to attain ultimately to a value of $-20°$.

Thus the rotation of this ester, whose specific rotation in the pure condition is only $+7{\cdot}8°$, can be made to vary from $+41°$ to $-20°$ by solution in these solvents; clearly, therefore, care must be taken in reporting the exact circumstances under which any rotation has been measured, and also in utilising rotation data obtained by the use of several different solvents. The curves also show that if an active compound is solid, so that its rotation in the homogeneous liquid condition cannot be determined, this value may still be arrived at by extrapolation from the data for its solutions, preferably in a number of solvents, the accuracy with which the extrapolation could be made depending, of course, on the solubility of the compound.

Influence of Various Solvents on the Rotation of Ethyl Tartrate.

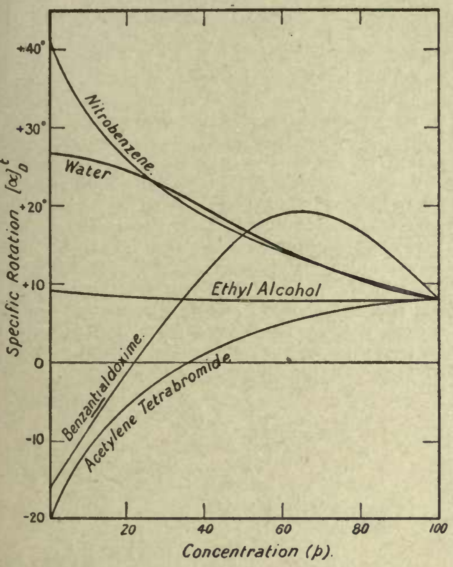


Fig. 36.

Many attempts have been made to explain these remarkable effects. Naturally a correlation has been suggested between the rotation and the osmotic molecular weight of the dissolved substance, but it has proved impossible up to the present to establish any connection. (*See* Frankland and Pickard, Chem. Soc. Trans. 1896, 69, 131; Patterson, *ibid.* 1901, 79, 182; 1902, 81, 1111; Ber. 1905, 38, 4049; 1908, 41, 113; Patterson and Thomson, *ibid.* 1907, 40, 1244; Walden, *ibid.* 1905, 38, 389; 1906, 39, 658; 1907, 40, 2463; Purdie and Irvine, Chem. Soc. Trans. 1904, 85, 1055.)

Another proposal, originally made by Tammann, was that the rotation depends upon the internal pressure of the solvent or of the mixture of solute and solvent. This idea was applied by Patterson (Chem. Soc. Trans. 1901, 79, 188) in the case of ethyl tartrate in various solvents, but instead of calculating the internal pressure, the molecular solution-volume of the ethyl tartrate at infinite dilution in the different solvents was determined, the assumption being made, as a first approximation, that all the change of volume suffered in the process of solution might be attributed to the solute, and further, that the magnitude of the solution-volume might be regarded as a measure of the internal pressure. Although these assumptions are not generally admissible, it is nevertheless possible that in some instances they may be nearly fulfilled. In any case experiment discovered a parallelism between the magnitude of the specific rotation and the molecular solution-volume, both at infinite dilution, as is illustrated in the following table (Ber. 1905, 38, 4101).

TABLE X.—ROTATION AND SOLUTION-VOLUME OF ETHYL TARTRATE IN VARIOUS SOLVENTS.

(Ethyl tartrate, M.V. = 170·9 c.c.)

Solvent	$[\text{M.S.V.}]^{20}$ infinite dilution	$[\alpha]^{20}_D$ infinite dilution
Water . .	160·1	+26·85°
Methyl alcohol .	159·3	+11·50
Glycerol . .	163·3	+10·57
Ethyl alcohol .	164	+9·13
n-Propyl alcohol	167·5	+7·40
iso-Butyl alcohol	170·3	+6·53
sec-Octyl alcohol	174·3	+5·24
Benzene . .	175·1	+6·1
Toluene . .	174·8	+4·6
o-Xylene . .	176·8	+2·7
m-Xylene . .	176·5	+1·8
p-Xylene . .	176·1	+0·7
Mesitylene .	177·4	−3·0
Chloroform .	178	−3·2

Excepting for water, there appears to be a fairly close relationship between the values of these two magnitudes. The idea was taken up by Winther and applied to explain the change of rotatory power with variation of temperature. In certain cases it is found that there is a direct, linear relationship between the values of the rotation and the molecular volume either in the homogeneous condition or in solution. Thus, for example, the figures for homogeneous ethyl diacetyltartrate may be given.

TABLE XI.

t	$[\alpha]_D$	$\Delta[\alpha]_D$	v	Δv	k
56·8°	+4·37°	0·38	0·8906	0·0087	44
67·6	4·75	0·17	0·8993	0·0027	63
71·3	4·92	0·28	0·9020	0·0061	46
78·2	5·20	0·40	0·9081	0·0070	57
86·7	5·60	0·70	0·9151	0·0114	61
100	6·30		0·9265		

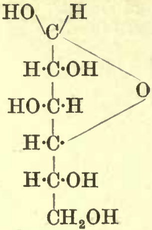
In the above table v is the specific volume, and k is a constant calculated from the equation:

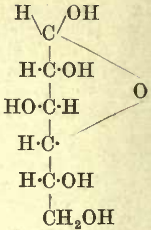
$$\Delta[\alpha]_D = k\Delta v.$$

The values of k vary irregularly about a mean value of 54, so that the rotation appears to be directly proportional to the specific volume. (For many other examples see Winther, Zeitsch. physikal. Chem. 1906, 55, 263.)

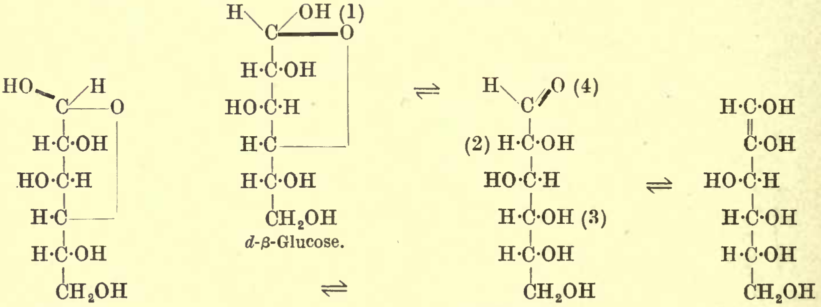
Muta-rotation. It not infrequently happens that the rotation of a compound, generally in solution, starting from a certain initial value gradually falls to reach a different end value. The substances which first attracted attention in this direction belong to the class of sugars, which rendered the matter of practical importance. When *d*-glucose is crystallised from 70 p.c. alcohol at the ordinary temperature, an anhydrous product is obtained, giving when dissolved in water, an initial specific rotation of about +109° which falls gradually to the constant value +53°. The solid form is called *d*-*α*-glucose. If, on the other hand, glucose be crystallised from water at a temperature above 98°, a solid, *d*-*β*-glucose, separates having a rotation initially of only +19° or thereabouts, the value being a little uncertain, as the substance is difficult to prepare in a pure condition. This rotation, too, changes slowly with lapse of time and ultimately also acquires the value +53°. Since the final rotation is almost half the highest value the phenomenon used to be called bi-rotation or semi-rotation, but is now generally referred to, on the suggestion of Lowry, as muta-rotation. A similar behaviour is found for fructose, galactose, lactose, maltose and other sugars.

The two varieties of glucose in the solid condition may be represented by the formulæ:


d-*α*-Glucose.


d-*β*-Glucose.

in which, however, the relative positions of the hydrogen atom and the hydroxyl group attached to the uppermost carbon atom are not definitely known.[1] When one of these compounds is dissolved in water a change might take place in two essentially different ways. Emil Fischer (Ber. 1890, 23, 2626) suggested that the molecule may become hydrated, the final constant value of the rotation being that of the hydrate. Lowry, however (Chem. Soc. Trans. 1899, 75, 213; 1904, 85, 1541, 1551), from analogy with the rotation changes which take place in nitrocamphor in non-aqueous solutions, in which there can be no hydration, attributes the change to an isodynamic process or perhaps to two such processes:


d-*α*-Glucose. *d*-*β*-Glucose. Aldehyde form. Enol form.

In solution the compound of constant rotation may have the true aldehyde formula or it might have the enolic structure, the presence of which last seems necessary to account for the readiness with which glucose in faintly alkaline solution is converted into a mixture of glucose, fructose and mannose. On dissolving *d*-*β*-glucose in water, the hydrogen atom marked (1) may wander to the lactonic oxygen atom, the uppermost carbon atom of the *d*-*β*-glucose molecule thus losing its asymmetry to give the inactive group $\underset{|}{\mathrm{H{\cdot}C{=}O}}$ of the aldehyde form. If now this hydrogen atom passes back again from its position (3) and attaches itself to the aldehydic oxygen atom (4) by the bond indicated by the thick line, it will yield *d*-*α*-glucose, in which the asymmetry of the uppermost carbon atom is the opposite of that found in *d*-*β*-glucose. If the hydrogen atom (2) of the aldehyde form wanders to the oxygen atom (4), both of the upper carbon atoms lose their asymmetry and the enolic form results, which presumably may pass back again through the aldehyde form into *d*-*α*-glucose or *d*-*β*-glucose or into the two forms of fructose or mannose respectively.

Influence of Temperature Change on Rotation in Solution.

Alteration of the temperature of a solution is generally accompanied, as in the case of a homogeneous compound, by a corresponding alteration in rotation. The case of ethyl tartrate has been examined fairly completely and the curves of Fig. 37 will help to explain the results obtained; the thick graph represents the change of rotation of the undiluted ester.

In a solvent such as acetylene tetrachloride, $p=9{\cdot}3$ which, at 20°, has a powerful depressing effect, the rotation rises rapidly with increase of temperature, whilst in a solvent like *α*-nitronaphthalene, $p=5$, which greatly raises the rotation of the ester, rise of temperature diminishes the rotation with almost equal rapidity. Other solvents, or the same solvents at intermediate concentrations, produce effects lying between these extremes, in such a manner that, roughly speaking, the whole series of curves gives the impression of a gradual variation of some property irrespective of the chemical composition of the solvents. It is interesting that, whilst the maximum rotation of the homogeneous ester lies at a temperature of 175°, it is again quite apparent in a solution in *m*-dinitro-benzene of $p=49{\cdot}6$, but at a lower temperature, 123°. The curve for *p*-nitrotoluene, $p=20$, shows a maximum at about 85°, and, from the appearance of the other curves, the maximum passes rapidly to lower temperatures as the rotation increases. It seems likely that other substances closely related to ethyl tartrate would behave in solution in a very similar manner.

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[1] See E. F. Armstrong: The Simple Carbohydrates and the Glucosides (Longmans, 1910), p. 64.

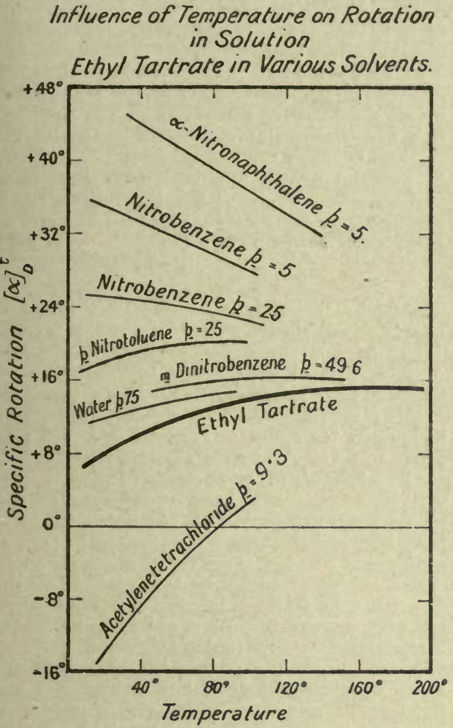

FIG. 37.

Rotation of active salts in solution. In 1873, Landolt (Ber. 1873, 6, 1077) observed that some of the neutral tartrates in aqueous solution had all very nearly the same specific rotation, whilst, later, Oudemans (Annalen, 1879, 197, 48, 66) showed that the rotation of dilute solutions of salts of quinamine seemed to be independent of the acid radicle. Hädrich (Zeitsch. physikal. Chem. 1893, 12, 476) applied the dissociation theory to the explanation of these results, suggesting that, as the solution of a salt is diluted, the rotation is modified because the active radicle becomes more and more dissociated from, and therefore less and less influenced by, the inactive radicle. In very dilute solutions, the rotation is that, merely, of the free active ion. Thus Landolt found the following data for solutions containing 7·69 grms. of tartaric acid in 100 c.c. Even in these by no means very dilute solutions the rotations lie fairly close together.

Neutral tartrate of	$[M]_D$
Lithium . . .	$+58{\cdot}1°$
Sodium . . .	59·9
Potassium . . .	64·4
Ammonium . . .	63·0

Again, Pope and Peachey (Chem. Soc. Trans. 1899, 75, 1086) give the following rotations for compounds formed by the combination respectively of dextro- and lævo- tetrahydroquinaldine with dextro-camphor-sulphonic acid.

Substance	$[M]_D$
$dC_{10}H_{13}N{\cdot}dC_{10}H_{15}O{\cdot}SO_3H$	$+173{\cdot}3°$
l———$\cdot l$———————	$-69{\cdot}5$

Half the difference between these, 121·4°, should be the rotation of a dilute solution of either form of tetrahydroquinaldine hydrochloride, and for the lævo variety experiment gave $-121{\cdot}7°$. Further, half the sum of the above, 51·9°, should be the rotatory power of ammonium camphor sulphonate, for which the value 51·7° was found. Use is occasionally made of this principle in determining the rotation of small quantities of active bases or acids, obtained by the resolution of potentially active compounds.

The truth of this Law of Oudemans, as it is called, has been questioned by F. L. Shinn (J. Phys. Chem. 1907, 11, 201).

The following table gives some data for ethyl tartrate and for nicotine, in regard to the relative effect of the same set of solvents on the rotation of a number of different active compounds.

TABLE XII.

Solvent	Ethyl tartrate $[\alpha]_D$ infinite dilution	Nicotine $[\alpha]_D$ infinite dilution
Formamide . .	$+30{\cdot}4°$	$-70°$
Water . .	26·85	77·4
Methyl alcohol .	11·5	129·4
Ethyl alcohol .	9·13	140·1
Benzene . .	6·1	163·5
Ethylene bromide	$-19{\cdot}1$	183·5

The sequence of the rotations in these different solvents is the same for both active compounds. *See also* Walden (Ber. 1905, 38, 345) for data bearing on this subject. Further work in this direction is desirable.

Mixed solvents. The effect of mixed solvents such, for instance, as a mixture of nitrobenzene and ethylene bromide on ethyl tartrate, or of water and calcium chloride on glucose, has been examined by Rimbach (Zeitsch. physikal. Chem. 1892, 9, 698; Rimbach and Weber (*ibid.* 1905, 51, 473); Patterson and Montgomerie (Chem. Soc. Trans. 1909, 95, 1128); Stubbs (*ibid.* 1911, 99, 2265); Patterson and Anderson (*ibid.* 1912, 101, 1833), but no generalisation seems to be possible as yet.

Combination of Active Solute with Inactive Solvent.

A suggestion often made to account for the variations of rotation observed in solution in what are termed 'indifferent' solvents, is that complex molecules of solute and solvent are formed, but the evidence advanced is usually of a negative character. An extensive research by Scheuer (Zeitsch. physikal. Chem. 1910, 72, 513), which included experiments on the viscosity, dilatation, melting-point, and rotation for light of various refrangibilities, of mixtures of ethyl diacetyltartrate, and menthol respectively, with a number of different solvents, failed to detect, either in the liquid or the solid phase, any sign of complex formation.

In some cases, however, combination certainly does occur. Thus Biot (Mém. de l'Acad. 1837, 16, 229; Ann. Chim. Phys. 1844, [iii.] 11, 82; 1850, 29, 341, 430; 1860, 59, 229) noticed that the addition of boric acid to solutions of tartaric acid greatly increased their rotation, and the same thing has been observed by Gernez for molybdates and tungstates (Compt. rend. 1887, 104, 783; 1888, 106, 1527; 1889, 108, 942). The addition of one molecular proportion of ammonium molybdate

$$[NH_4]_6Mo_7O_{24},4H_2O,$$

to a $c=2{\cdot}5$ solution of tartaric acid, raises the rotation, α_D^{17}, from $+0{\cdot}351°$ to $+15{\cdot}66°$. This principle is therefore occasionally employed in investigations where small quantities of active compounds are obtained, in order to increase the rotation and render it perceptible. These increases have only been observed for active oxy acids, and the method must be used with caution, since it was found by Gernez (Compt. rend. 1889, 109, 769) that whilst the addition of one molecular equivalent (2·017 grms.) of sodium molybdate, $Na_2MoO_4,2H_2O$ to malic acid solution, $c=9{\cdot}97$, raised α_D^{17} from $-0{\cdot}189°$ to $+13{\cdot}26°$, the addition respectively of 1·4, 2·85, 4·25 grms., gave in each instance an inactive solution, maximum and minimum rotations occurring at intermediate concentrations. Compounds of this type and also those containing arsenic and antimony have been examined by G. G. Henderson with Prentice (Chem. Soc. Trans. 1895, 67, 1035), Barr (*ibid.* 1896, 69, 1452) and Orr and Whitehead (*ibid.* 1899, 75, 548) not only with malic acid but also with lactic acid, whilst Walden (Ber. 1897, 30, 2889) uses alkaline uranyl nitrate for producing strongly active compounds of the same type.

Rotation dispersion. The determination of the rotation for light of different wave-lengths may be carried out either with approximately monochromatic sources of light, such as a flame containing incandescent salts of sodium, lithium, thallium, indium, or that from a mercury arc lamp, the light being purified by means of some coloured solution which absorbs the rays not required. (See, for example, Winther, Zeitsch. physikal. Chem. 1902, 41, 161; Scheuer, *ibid.* 1910, 72, 513.) It is, however, better to purify white light or that from any of the sources mentioned, by means of a spectroscope, placed at either end of the polarimeter.

Results similar to the following are then obtained:

Fraunhofer line	B	C	D	E	F	G
Wave-length	686·7	656·2	589·2	526·9	486·1	430·7
Quartz[1] α [1 mm.]	+15·75°	17·31°	21·71°	27·54°	32·76°	42·59°
Sucrose[2] $[\alpha]$	+47·56	52·70	66·40	84·56	101·81	131·96

The ratio of the values for light of any two wave-lengths is termed the dispersion coefficient, and in the above cases, taking the B line as unit, the dispersion coefficients would be as follows:

Fraunhofer line	B	C	D	E	F	G
Quartz . .	1	1·09	1·38	1·75	2·08	2·70
Sucrose .	1	1·11	1·40	1·78	2·13	2·77

The dispersion of quartz is practically the same as that of a cane sugar solution—a sucrose solution which has the same rotation as a certain quartz plate for any one ray will have the same rotation as the quartz plate for all rays, which makes it possible to use quartz wedge compensation instruments for the determination of the rotation of sugar solutions.

For the relationship between the rotation and the wave-length of the light used, Boltzmann (Pogg. Ann. Jubelb. 1874, 128) has proposed the equation

$$\alpha=\frac{A}{\lambda^2}+\frac{B}{\lambda^2},$$

in which, from the above observations on quartz, $A=7{\cdot}108293\times10^{-6}$ and $B=0{\cdot}1477086\times10^{-12}$. For the sugar solution $A=2{\cdot}16036\times10^{-5}$ and $B=5{\cdot}47276\times10^{-13}$. Winther (Zeitsch. physikal. Chem. 1902, 41, 182) suggests another expression, which agrees better with his results for esters of tartaric acid and may prove to be of a more suitable form.

In a number of compounds such as quartz, and in sucrose solutions, the dispersion coefficients do not vary with change of temperature, and in numerous cases also the dispersion coefficients are the same for the homogeneous active substance as for its solutions, when the dispersion is said to be normal. Sometimes, however, as was first observed for solutions of tartaric acid by Biot (Mém. de l'Acad. 1838, 15, 93), the magnitude of the rotation does not increase constantly as the wave-length of the light used diminishes, but reaches a maximum at some intermediate wave length and then decreases again. Winther (Zeitsch. physikal. Chem. 1902, 41, 177) finds this to occur also in homogeneous compounds, such as the methyl, ethyl and *n*-propyl esters of tartaric acid and the same holds for ethyl diacetyltartrate (Scheuer, *ibid.* 1910, 72, 587).

Fig. 38 represents data obtained by Winther (*l.c.*) for the first three simple esters of tartaric acid, at a number of different temperatures, the dispersion being abnormal in all cases. The maximum rotation for methyl tartrate occurs in the neighbourhood of the yellow light, but as the temperature rises the maximum shows a tendency to shift towards the violet; this is clearly more pronounced amongst the curves for ethyl tartrate, and so much so in those for *n*-propyl tartrate that at 70° the dispersion has almost become normal. It is of interest that, just as has already been observed in regard to the effect of temperature change on rotation in solution (Fig. 37), the set of curves for these three homologous esters seems to form a complete whole; some property appears to progress gradually throughout the diagram, irrespective of the nature of the chemical compound used. The alteration of dispersion for the three esters is closely analogous, so that if methyl tartrate be heated until it has a rotation of, say, $\alpha°$ for the red rays, its dispersion curve at that temperature will be the same as that for ethyl tartrate at the temperature at which its rotation is also $\alpha°$ for red light, the same curve being obtained for *n*-propyl tartrate at some other temperature. The dispersion curve for ethyl tartrate, for example at 72°, is coincident with the dispersion curve for *n*-propyl tartrate at 19°; so far as this property is concerned, ethyl tartrate at 72° seems to be the same thing as *n*-propyl tartrate at 19°.

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[1] Soret and Sarasin, Compt. rend. 1882, 95, 635.

[2] Cane sugar in water, $p=10$–30, Stefan, Wien. Sitz. Ber. 1866, 52, ii. 486.

Rotation Dispersion of Methyl, Ethyl and n Propyl Tartrate at Different Temperatures.

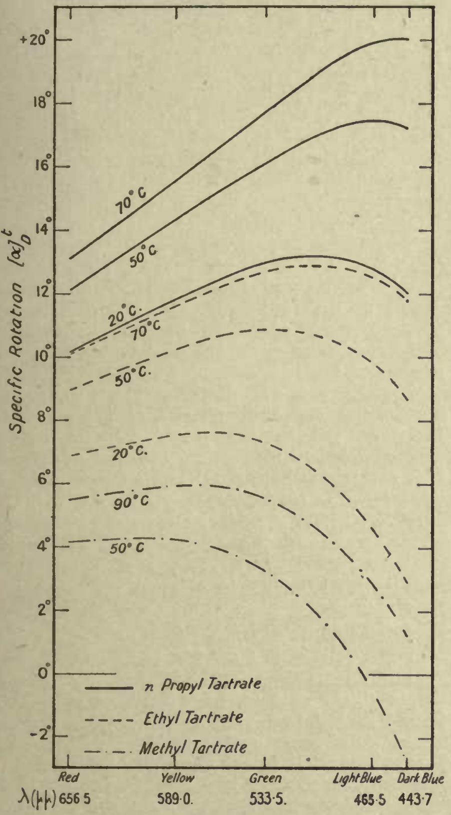


Fig. 38.

For a photographic method of determining dispersion into the ultra-violet, see Lowry, Proc. Roy. Soc. 1908, A. 81, 472.

Magnetic rotation. Faraday discovered in 1845 that the plane of polarisation of light passed through transparent matter of any kind in a magnetic field in the direction of the lines of force, is altered to an extent proportional to the strength of the field, the thickness of the layer of substance traversed, and the nature of the light used. If the field is produced by a current flowing round a coil, the direction of rotation of the plane of polarisation is generally positive for diamagnetic substances and negative for magnetic substances, the positive direction being that in which the current producing the field flows, without reference to the direction of the ray. Thus if the field be produced by a current flowing in the counter-clockwise direction relative to the observer, the rotation of a positive substance will be also in a counter-clockwise direction, and if the beam be reflected back through the substance the plane of polarisation will be again deflected in the same direction as before, so that the angle of rotation after passing back and forwards through the substance will be doubled. Magnetic rotation thus differs very markedly from permanent rotation.

From the chemical point of view this phenomenon has been developed almost exclusively by the late Sir W. H. Perkin, in a series of very comprehensive papers (Chem. Soc. Trans. 1882, 41, 330; 1884, 45, 421; 1896, 69, 1025; 1906, 89, 608; 1907, 91, 806 and others).

Perkin's method consists in determining the magnetic rotation of water and then under the same circumstances of field, &c., the magnetic rotation of some other substance, the current being reversed after each observation and the mean of the sum taken. Each rotation is then divided by the corresponding density, the value thus found for the substance as compared with that for water taken as unity being the specific magnetic rotation of the substance. The specific rotation multiplied by the molecular weight gives the molecular magnetic rotation.

In ascending a homologous series, the molecular magnetic rotation increases by a constant amount for each CH_2 group added, and definite values may be obtained for certain groups or atoms so that, knowing the constitution of a compound, its molecular magnetic rotation can be calculated. Perkin applied this method as a criterion for the determination of the constitution of certain substances which presented difficulty. Thus, for example, he found (Chem. Soc. Trans. 1902, 81, 294)

Substance	Molecular magnetic rotation
Hexane . . .	6·646
Hexamethylene .	5·664

the difference between these values (—0·982) being that due to ring formation and loss of two atoms of hydrogen. In his last paper (*ibid.* 1907, 91, 807) he quotes:

Magnetic rotation of hexatriene .	12·196
Difference due to ring formation .	—0·982
	11·214

The sum, 11·214, should be the rotation of benzene, which is, in fact, 11·284. There is little doubt that magnetic rotation is one of the most definitely constitutive properties that we know, but, owing to the elaborate and costly character of the apparatus required and the unremitting attention necessary in carrying out observations, it has been used by few other workers.

In addition to the original papers quoted in this article, the following books may be consulted for fuller details regarding most of the matters dealt with:—H. Landolt, Das optische Drehungsvermögen organischer Verbindungen, 1898; the same, translated, with additions to date, by J. H. Long, The Optical Rotating Power of Organic Substances, 1902; J. H. van't Hoff, The Arrangement of Atoms in Space, translated by A. Eiloart, 1898; A. Werner, Kurzes Lehrbuch der Stereochemie, 1904; A. W. Stewart, Stereochemistry, 1907.

T. S. P.

POLIANITE *v.* PYROLUSITE.

POLONIUM (*Radium F; Radiotellurium*). At.wt. =approx. 210 (?).

A radioactive element, discovered by P. and M. Curie in the residues obtained from pitchblende after the mineral had been roasted with sodium carbonate and the product extracted with sulphuric acid to dissolve uranium salts. The insoluble residue, from which radium was originally prepared, was found to contain another radioactive element which was precipitated together with bismuth sulphide by sulphuretted hydrogen in acid solution (Compt. rend. 1898, 127, 175). The further separation of the active body from bismuth was effected by the following methods: (1) sublimation of the sulphides at 700° *in vacuo*, the active sulphide being the more volatile; (2) precipitation of the basic nitrates from solution, the active material precipitating first; (3) precipitation of a strongly acid chloride solution with hydrogen sulphide, the active sulphide separating first. (For the preparation of polonium compounds *v.* also Giesel, Ann. Chim. Phys. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608; 1903, 36, 728, 2368; 1908, 41, 1059; Marckwald, Ber. 1902, 35, 2285; Curie and Debierne, Compt. rend. 1910, 150, 386.)

In 1902, Marckwald (Ber. 1902, 35, 2285, 4239; 1903, 36, 2662) obtained a radioactive substance associated with tellurium, which he called *radiotellurium*. This is almost certainly identical with polonium, as Debierne soon afterwards pointed out (Compt. rend. 1904, 139, 281). Although Marckwald (Jahrb. Radioaktiv. Elektronik. 1905, 2, 133) disputed their identity, he subsequently (Chem. Zentr. 1906, ii. 412) recommended that his material should be called polonium.

Polonium has been found in the uranium mineral carnotite (Friedel and Cumenge, Compt. rend. 1899, 128, 532).

When a plate of bismuth is immersed in a polonium solution, the active matter is deposited on the plate; the active material is also precipitated by stannous chloride (Marckwald).

The radiation from polonium is extremely active, consisting entirely of α-rays identical with those of radium (Becquerel, Compt. rend. 1903, 136, 431, 977). The rays are deflected in a strong magnetic field (Mackenzie, Phil. Mag. 1905, [vi.] 10, 538; Ewers, Chem. Zentr. 1906 i. 1084). The range of the α-particles in air is 3·8 cms. (Levin, Amer. J. Sci. 1906, [iv.] 22, 8; *cf.* Aschkinass, Annalen Physik. 1908, [iv.] 27, 377). The activity of polonium decays according to the usual exponential law, the half-period being 140 days (Curie, Compt. rend. 1906, 142, 273). The half-period for radiotellurium is 139·6 days (Greinacher and Herrmann, Jahrb. Radioaktiv. Elektronik. 1905, 2, 136).

Owing to the minute quantities of polonium available it has been extremely difficult to detect helium as one of its disintegration products, but Curie and Debierne (Compt. rend. 1910, 150, 386) have obtained 1·3 c.mm. of helium from approximately 0·1 mgm. of polonium (*cf.* Greinacher and Kernbaum, Zeitsch. physikal. Chem. 1907, 8, 339). The spectrum lines $\lambda=4642$, 4170·5, 3913·6, 3652·1 probably belong to polonium. Polonium preparations slowly evolve heat (Duane, Compt. rend. 1909, 148, 1665).

Polonium has been identified with radium F, the last of the series of transformation products of radium that has been recognised. The change from radium to radium F involves the loss of four α particles from the atom. The atomic weight of polonium should therefore be about 210. The unknown radium G, into which polonium disintegrates, is devoid of sensible radioactivity, since the half period of polonium preparations that have been kept for five years is practically identical with the figure given above (Waters, Phil. Mag. 1910, [vi.] 19, 905). Radium G will probably prove to be lead.

The *radio-lead* of Hofmann and Strauss (Ber. 1901, 34, 3033; Hofmann and Wolff, *ibid.* 1903, 36, 1040) has been shown to owe its activity to the presence of the transformation products *radium D, E* and *F*. The substance *β-polonium*, described by Giesel (Ber. 1906, 39, 780) was shown later to be radium E (Giesel, *ibid.* 1906, 39, 1014).

POLYBASITE. A sulphantimonite of silver (60–72 p.c.) and copper (3–15 p.c.) with the formula $8(Ag,Cu)_2S\cdot(Sb.As)_2S_3$ (F. R. Van Horn, Amer. J. Sci. 1911, 32, 40). The antimony may be partly or wholly replaced by arsenic, forming a passage to the isomorphous species *pearceite*: small amounts of zinc and iron are also often present. Both minerals occur as iron-black, six-sided plates with monoclinic symmetry. They are found in the silver-mining districts of Mexico, Colorado, Nevada, &c., sometimes in sufficient abundance to be of importance as ores of silver. L. J. S.

POLYCHREST SALT. An old name for normal potassium sulphate; applied also sometimes to Rochelle salt.

POLYCHROMINE *v.* PRIMULINE AND ITS DERIVATIVES.

POLYGALIC ACID *v.* SENEGA.

POLYGONIN *v.* GLUCOSIDES.

POLYGONUM CUSPIDATUM. *P. cuspidatum* (Sieb. et Zucc.), is common in India, China, and Japan, and is referred to by A. Henry in a paper entitled 'Chinese Names of Plants' (Journal Royal China Branch of Royal Asiatic Society, 22, New Series, No. 5, 1887) as 'Kan-yen, wu-tzu,' the name at Patung for the root of the *P. cuspidatum*, which is said to be used for dyeing yellow.

According to Perkin (Chem. Soc. Trans. 1895, 67, 1084), the main constituent of this root is a glucoside *polygonin* $C_{21}H_{20}O_{10}$, forming orange-yellow needles, m.p. 202°–203°, which, when hydrolysed by acids, gives *emodin* and a sugar.

$$C_{21}H_{20}O_{10}+H_2O=C_{15}H_{10}O_5+C_6H_{12}O_6.$$

A trace of a second glucoside is also present, from which the *emodin monomethylether*, m.p. 200°, previously found to exist in the root bark of the *Ventilago madraspatana* (Gaertn.) (Chem. Soc. Trans. 1894, 65, 932) was obtained.

A. G. P.

POLYHALITE. A triple sulphate,

$$K_2SO_4\cdot MgSO_4\cdot 2CaSO_4,2H_2O,$$

occurring in some abundance in salt deposits. In the potash-salt beds of Stassfurt in Prussia and Stebnik in Galicia it is more closely associated with rock-salt, anhydrite, and gypsum; and it is also found with these minerals in the salt mines of Ischl, Ebensee, Aussee, Hallstatt, and Hallein in Austria, Berchtesgaden in Bavaria, Vic in Lorraine, and Varangéville near Nancy. The mineral occurs as nodules with a fibrous or platy structure and a brick-red colour, this colour being due to the enclosure of iron hydroxide, On the artificial production of polyhalite, *v.* J. H. van't Hoff, Sitz. Akad. Wiss. Berlin, 1906, 412 (*v.* POTASSIUM).

L. J. S.

POLYMERISED OILS *v.* OILS, FIXED, AND FATS.

POMEGRANATE, *Punica granatum* (Linn.). The fruit is edible. It consists of a hard and thick rind, filled with a pulp containing numerous seeds. König gives, as the composition of the pulp—

Water	Protein	Invert sugar	Cane sugar	Other N-free ext.	Acid	Fibre and seed	Ash
79·3	1·2	11·0	0·7	3·8	0·8	2·8	0·5

Analyses of the juice of pomegranates by Borntrãger and Paris (Bied. Zentr. 1899, 28, 198) show that in ripe fruit, the juice contains from 0·37 to 0·51 grm. of acid and from 10·5 to 13·69 grms. of reducing sugar per 100 c.c.; in unripe fruit the free acid amounted to from 3·0 to 3·4 grms., the reducing sugar to from 7·8 to 11·3 grms. The must easily ferments and yields a wine with the flavour of raspberries, containing from 4·4 to 7·0 grms. of alcohol per 100 c.c.

The bark of the stem and roots is used in medicine as an astringent and anthelmintic. The root bark is the richer in the active principles—the alkaloids—*pelletierine, isopelletierine, pseudo-pelletierine* and *methyl-pelletierine.* The first two, constituting usually from 40 to 50 p.c. of the total alkaloids present, are of value as vermifuges: the last two have little or no effect.

The total amount of alkaloids in the bark of the roots grown in the south of France is about 0·6–0·7 p.c., while in the bark of the branches about 0·5 p.c. is present (Ewers, Arch. Pharm. 1899, 237, 49). In the products from Java, the figures were higher (Beckurts, *ibid.* 1900, 288, 8). The alkaloids were first obtained by Tanret (Compt. rend. 1878, 86, 1270) who found pelletierine $C_8H_{15}NO$ to be a colourless liquid, boiling (with decomp.) at 195°, with a sp.gr. of 0·988, soluble in 20 times its vol. of water: its salts are lævorotatory.

iso-Pelletierine is also a liquid of similar composition but is optically inactive; *pseudo*-pelletierine $C_9H_{15}NO$ is a crystalline solid, methyl-pelletierine $C_9H_{17}NO$ is a liquid boiling at 215°, soluble in 25 parts of water and yielding salts which are very deliquescent.

The alkaloids of pomegranate bark have been studied by Ciamician and Silber (Ber. 1892, 25, 1601; *ibid.* 26, 156; 26, 2738; 1894, 27, 2850); Piccini (Gazz. chim. ital. 1899, i. 408; ii. 311), and Willstätter and Veraguth (Ber. 1905, 38, 1984). The rind of the fruit contains a yellow colouring substance—probably ellagic acid (A. G. Perkin, Chem. Soc. Trans. 1897, 71, 1137). H. I.

POMEGRANATE RIND *v.* TANNINS.

PONCEAU *v.* AZO- COLOURING MATTERS.

PONCEAU CRYSTAL *v.* AZO- COLOURING MATTERS.

POPLAR BUDS. *Chrysin* $C_{15}H_{10}O_4$ is contained in the leaf buds of the poplar (*Populus pyramidalis* (Salisb.), *P. nigra* (Linn.), *P. monilifera* (Ait.)), in which it is present to the extent of about ¼ p.c. It was first isolated by Piccard (Ber. 6, 884, 1160; 7, 888; 10, 176) and is best prepared by the method devised by this chemist.

An alcoholic extract of 1000 grams of poplar buds is treated while hot with about 120 grams of lead acetate, and after standing for some time the yellow precipitate is removed. Through the clear filtrate sulphuretted hydrogen is passed in order to decompose lead salts, the sulphide of lead is filtered off and the liquid evaporated to dryness: The residue dissolved in a little hot alcohol gradually deposits crystals of chrysin, which are collected, successively extracted with carbon disulphide, benzene, and boiling water, and finally crystallised two or three times from alcohol.

Pure chrysin crystallises in colourless leaflets, m.p. 275°, and dissolves in alkaline solutions with an intense yellow colouration. When acetylated, *diacetylchrysin* $C_{15}H_8O_4(C_2H_3O)_2$, colourless needles, m.p. 185°, is produced, but by the action of methyl iodide in the usual manner a *monomethylether* $C_{15}H_9O_3{\cdot}OCH_3$, m.p. 163°, only can be prepared. The latter yields *acetylchrysinmonomethylether*

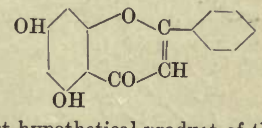
$$C_{15}H_8O_3(OCH_3)C_2H_3O,$$

colourless needles, m.p. 149°, and with alcoholic soda gives a bright yellow sodium salt which is decomposed by washing with water (*v.* Kostanecki, Ber. 1893, 26, 2901).

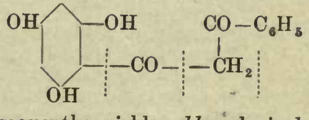
When digested with boiling concentrated potassium hydroxide solution, chrysin gives *phloroglucinol, benzoic acid, acetic acid* and *acetophenone* (Piccard, *l.c.*), the last-named in very small quantity and the reaction can be expressed as follows:

$$C_{15}H_{10}O_4+3H_2O =C_6H_6O_3+C_6H_5COOH+CH_3{\cdot}COOH$$

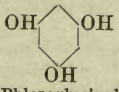
An investigation by Kostanecki (*l.c.*) indicates that chrysin is a *dihydroxyflavone* and possesses the constitution



The first hypothetical product of the hydrolysis of chrysin by means of alkali (compare flavone) is 2 : 4 : 6 - trihydroxybenzoylacetophenone



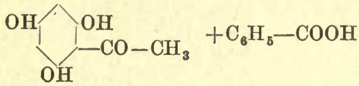
which subsequently yields *phloroglucinol* and *acetophenone* and *carbon dioxide*



$+CO_2+CH_3{\cdot}CO{\cdot}C_6H_5$

Phloroglucinol. Acetophenone.

On the other hand, *phloroacetophenone* (which is unstable in the presence of alkali and is thereby converted into phloroglucinol and acetic acid) and benzoic acid may also be produced.

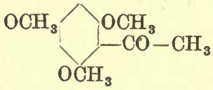


Phloracetophenone. Benzoic acid.

Chrysin has been synthesised by Emilewicz, v. Kostanecki and Tambor (Ber. 32, 2448) in the following manner.

Phloroacetophenonetrimethylether (1) gives, when treated with ethyl benzoate in the presence of sodium, 2:4:6-*trimethoxybenzoylacetophenone* (2).

(1)



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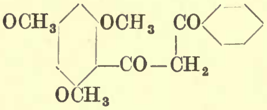

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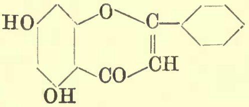


The latter, when digested with strong boiling hydriodic acid, is demethylated and ring formation occurs with the production of chrysin (3).

The following derivatives of chrysin have been prepared.

Dibromchrysin $C_{15}H_8Br_2O_4$ (Piccard, Ber. 1873, 6, 886); *Di-iodochrysin* $C_{15}H_8I_2O_4$, yellow needles (Piccard); *Dinitrochrysin* $C_{15}H_8(NO_2)_2O_4$, red leaflets, m.p. 272° (Piccard and Darier, Ber. 1894, 27, 21); *Chrysinmonoethylether*

$C_{15}H_9O_3(OC_2H_5)$,

thin needles (m.p. 146°) (Piccard); *Chrysin*iso*amylether* $C_{15}H_9O_3(OC_5H_{11})$, thin needles, m.p. 125° (Piccard); *Dibromchrysin*iso*amylether*

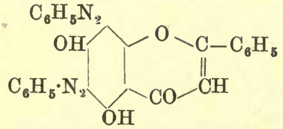
$C_{15}H_7Br_2O_2(OC_5H_{11})$

needles, and *dinitro-diacetylchrysin*

$C_{15}H_6O_4(NO_2)_2(C_2H_3O)_2$

yellow needles, m.p. 229° (Darier, *l.c.*).

Disazobenzenechrysin (Perkin, Chem. Soc. Trans. 1896, 69, 1439)



orange-red needles, m.p. 251°–252°, insoluble in alkaline solutions, is unaltered by prolonged digestion with acetic anhydride.

Chrysin is a feeble dyestuff. The shades produced on wool mordanted with aluminium, chromium and iron, are respectively pale bright yellow, pale yellow-orange, and chocolate brown.

Tectochrysin, a second constituent of poplar buds, is present in the benzene extracts from the crude chrysin. Tectochrysin is chrysin monomethylether ($C_{15}H_9O_3{\cdot}OCH_3$) (Piccard), and is identical with the methylation product of chrysin itself. A. G. P.

POPPY SEED OIL. Poppy seed oil is obtained from the seeds of the two varieties of poppy, *Papaver somniferum* (Linn.), viz. *P. album* and *P. nigrum* (DC.), by pressing. The plant is grown extensively in Asia Minor, Persia, India, Egypt, South Russia, and the North of France. The seeds yield from 45–50 p.c. of oil. The seed produced in Manchuria is grown together with other wild seeds yielding about 16 p.c. of a non-drying oil; hence the Manchurian oil is of very low quality as regards drying powers.

In France a distinction is made between *huile d'œillette* and *huile de pavot.* The former is obtained from indigenous, or at any rate European, poppy seed, whilst the name *huile de pavot* is given to the oil obtained from oversea seed. Since by far the greatest part of expressed oils, both of European as also of oversea origin, is used as a table oil, all edible poppy seed oils are termed *huile d'œillette.*

The 'cold drawn' oil, the oil of the first expression, is almost colourless or very pale golden yellow; this is the 'white poppy seed oil' of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the 'red poppy seed oil' of commerce.

'Sweet' (fine) table oils prepared by cold expression in Marseilles and in the north of France (in Lille, Arras, Douay, Cambrai). The cold-pressed oil is filtered before being placed on the market. In some of these establishments paper filters are said to be used even at present.

Poppy seed oil has little or no odour and a pleasant taste, so that it is largely used as salad oil, especially as it does not easily turn rancid. The oil of unsound quality, however, possesses an acrid taste.

The cakes resulting as a by-product are rich in nitrogen and are fed to cattle; only when the cakes have become mouldy are they employed as a manure for early fruit.

For the chemical and physical characteristics, see tables under Oils, Fixed, and Fats.

Poppy seed oil is, as a rule, contaminated with small quantities of sesamé oil, owing to the seed being usually expressed in the same works in which sesamé oil is produced. Edible poppy seed oil is at present frequently adulterated with sesamé oil and also with hazelnut oil to improve the taste of the edible oil obtained from stored seeds.

The differentiation of poppy seed oil from walnut oil is of importance in the examination of white paints. The readiest means for this purpose is furnished by the bromide test (see Oils, Fixed, and Fats). Walnut oil yields from 1·4 to 1·9 p.c. of ether-insoluble brominated glycerides, whereas poppy seed oil yields none.

J. L.

POPULIN (*Benzoyl salicin*) $C_{20}H_{22}O_8,2H_2O$ is a glucoside contained in the bark and leaves of the Poplar, *Populus tremula* (Linn.), from which it is extracted by boiling the leaves with water. The extract is precipitated with lead acetate and the filtrate is treated with sulphuretted hydrogen, after which it is decolourised with charcoal, evaporated and recrystallised (Piccard, Ber. 1873, 6, 890; Hallwachs, Annalen, 1857, 101, 372; Piria, *ibid.* 1855, 96. 376). It can be readily obtained also by the following process.

A solution of 20 grams of salicin in a litre of water is rendered alkaline with potassium hydroxide and 10 grams benzoyl chloride are added very slowly with constant stirring, more alkali being added from time to time so as to avoid the formation of much free acid. The populin separates as a bulky white precipitate, which is dried, powdered, and extracted with ether. The insoluble residue is recrystallised from boiling water and subsequently from hot alcohol (Dobbin and White, Pharm. J. 1904, 73, 233).

It forms colourless prismatic needles which lose their water of crystallisation at 100°, and melt at 180°. It has a sweetish somewhat acid taste, is lævorotatory (Biot and Pasteur, J. 1852, 179), is sparingly soluble in ether and in cold water but readily so in hot water and in alcohol.

When boiled with lime or baryta water it is decomposed into salicin and benzoic acid. With nitric acid it yields *benzohelicin* $C_{20}H_{20}O_8$, and in strong sulphuric acid it dissolves with a red colour. When boiled with dilute acids it yields *saliretin*, benzoic acid and glycose (Lippmann, Ber. 1879, 12, 1649). *V.* Glucosides.

PORCELAIN *v.* Pottery.

PORCELAIN CLAY *v.* Clay.

PORCELAIN STONE *v.* Clay.

PORPEZITE. A native alloy of gold and palladium.

PORPHYRY. A term loosely applied to any rock in which distinct crystals are embedded in a fine-grained ground-mass. The structure is well seen in many igneous rocks, where crystals have consolidated from a molten magma before the eruption of the mass. The typical porphyry of the ancients, *lapis purpureus*, contains crystals of white or pink felspar in a *purple*, crimson, or chocolate-coloured base, whence the original name πορφυροῦς or πορφυρίτης λίθος. It was extensively quarried by the Romans at Jebel Dokhan ('Mountain of Smoke'), in eastern Egypt, a locality described by Latin writers as *Mons porphyrites*; but although regarded as the most sumptuous of decorative stones, and largely used by Roman architects and sculptors for pillars, pavements, busts, and sarcophagi, it appears to have been unworked by the ancient Egyptians.

The crystals in the ancient red porphyry were analysed by Delesse, who found them to be a lime-soda plagioclase (Bul. Soc. Géol. France, 2 sér. 7, 484). The crypto-crystalline ground-mass contains much felspar altered to a reddish manganiferous epidote (withamite). The red colour of the rock is mainly due to the large quantity of finely divided hæmatite (J. Couyat, Compt. rend. 1908, 147, 988). Beautiful crystals of hornblende occur in the ancient red porphyry, and the rock may be described as a *hornblende-porphyrite*. The history of the rock has been fully worked out by O. Schneider (Ueber den roten Porphyr der Alten, Dresden, 1887). The Egyptian quarries have been visited and described by Williamson and other travellers (*v.* W. Brindley, Trans. R. Inst. Brit. Architects, 1888). Red porphyry, somewhat similar to the Egyptian, but less beautiful, occurs in the Sinaitic peninsula, at Elfdalen in Sweden, and in Siberia. The *porfido rosso antico* of Egypt is to be clearly distinguished from *rosso antico*, or the ancient red marble of Laconia.

The green porphyry of the ancients (*porfido verde antico*), known to Italian antiquaries as *serpentino*, was worked at Mount Taygetus in the Morea, and termed *lapis Lacedæmonius*. It contains white, or pale-green, crystals of plagioclase, embedded in a ground-mass filled with viridite, or chloritic products of the alteration of ferro-magnesian silicates. A similar, but less handsome, stone is the diabase-porphyrite of Lambay Island, near Dublin; the Lake District of Cumberland also yields a similar rock.

The *quartz-porphyries*, belonging to the acid group of igneous rocks, and known in Cornwall as *elvans*, contain well-developed crystals of quartz, and often also of felspar, embedded in a felsitic ground-mass, consisting of a minutely crystalline aggregate of felspar and quartz. The elvans are sometimes worked as ornamental stones. Many granite rocks are beautifully porphyritic, and some of the Cornish granites owe their character to the presence of bold crystals of orthoclase. Fine crystals of pink and salmon-coloured orthoclase form the characteristic feature of the well-known porphyritic granite of Shap in Westmoreland, and of the handsome luxullianite of Cornwall. F. W. R.

PORPOISE OIL. Porpoise oil is obtained from the brown porpoise, *Delphinus phocœna* (Linn.). The oil from the blubber is kept separate from that prepared from the cavities in the head and from the jaw, exactly as in the case of dolphin oil (*see* Oils, Fixed, and Fats tables). Hence we differentiate between *body oil* and *jaw oil*.

Both oils are characterised by the high proportion of volatile fatty acids they yield on saponification. The jaw oil contains much higher proportions of volatile acids than does the body oil. The oil is used, like dolphin oil, for lubricating delicate machinery, especially type-writing machines. J. L.

PORTLAND CEMENT *v.* Cements.

PORTUGALLO OIL. Essential oil of orange peel (*v.* Oils, essential).

POTASSIUM. Symbol K. At.w. 39·1.

Occurrence. Potassium occurs, principally as chloride and sulphate, in sea-water and other natural waters, a litre of the former containing from 0·5 to 0·7 gram of the element. As chloride or carbonate, or as an organic salt, it occurs in soils and vegetable and animal substances. Thus, wood ashes contain much potassium carbonate, which also forms a considerable proportion of the ash of marine plants, such as *laminaria* and *fuci*. Potassium occurs as *sylvine* or *sylvite* KCl, and as *carnallite* $KCl{\cdot}MgCl_2,6H_2O$, especially in the beds overlaying the great salt deposits of Stassfurt. As nitrate, it is found as an efflorescence on the soil, usually together with the sodium salt, in Peru, Chile, &c., and as an important constituent of many mineral waters, such as those of Harrogate and Vichy. As the double sulphate of aluminium and potassium, it occurs in *alumstone* or *alunite* $3Al_2SO_6{\cdot}K_2SO_4,6H_2O$, principally in trachyte and other rocks subjected to the action of sulphurous gases. It is found as bitartrate in wines, and as sulphate, carbonate, and chloride in beetroot molasses. As an organic salt (sudorate), it occurs in the 'suint' of sheep, and is separated therefrom as carbonate together with wool fat (Langbeck, J. Soc. Chem. Ind. 1890, 356).

The main source of potassium, however, is the primitive rocks, in which it occurs as *orthoclase* (potash felspar) $Al_2O_3{\cdot}K_2O{\cdot}6SiO_2$; *muscovite* (potash mica) $K_2O{\cdot}3Al_2O_3{\cdot}4SiO_2$, *leucite* $K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$; *apophyllite*

$$4(CaO{\cdot}2SiO_2{\cdot}H_2O)KF,$$

and other zeolites, and in many other silicates.

The sources from which potassium salts are obtained for technical purposes are—firstly, the sea-water; secondly, the mineral crust of the earth; thirdly, the vegetable, and to some extent the animal, kingdom.

The quantity of potassium salts contained in *sea-water* is not very large, but it has been found economically possible to extract it therefrom, as we shall see in the case of potassium chloride. Indirectly, the potassium salts obtained in the working up of kelp are derived from this source.

The *mineral crust of the earth* contains about 2·4 p.c. K_2O in the state of *silicates*, as a constituent of several of the most important minerals as felspar and mica; hence both older and younger rocks (granite, mica, slate, basalt, &c.) are sources of potash. By the decay of the rocks containing these minerals, potassium compounds have been spread all over the earth as part of the arable soil; from this source are derived, not only the potassium compounds contained in all plants, but probably most of those contained in sea-water. The importance of this occurrence of potash is enormous for the existence of all organisms; but it has not been possible so far to extract potassium compounds for technical purposes from the natural silicates or the arable soil in an economical way.

Several other salts of potassium are, however, more adapted for this purpose. Potassium *nitrate*, as found in the crude state, especially in India, is certainly more valuable in respect of its acid than of its alkaline constituent; but the latter is also very important, as is best proved by the large quantity of potassium chloride employed for the manufacture of artificial saltpetre.

Potassium sulphate occurs in large quantities in alum rock, and in several of the minerals found together with carnallite in the Stassfurt deposits.

Potassium chloride is found both in the pure state, as *sylvine*, and in much larger quantities as *carnallite*, in the Stassfurt deposits and some other places. This is at present the most important of all the sources from which potassium salts are obtained for technical purposes.

In the *vegetable kingdom* potassium is universally found, principally in the liquid contents of the cells and vessels, chiefly combined with organic acids. On burning it appears in the ashes as carbonate, together with more or less sulphate, chloride, phosphate, and silicate. It is unnecessary to say that all this potassium is derived from the soil on which the plants grow; but for many centuries, indeed, apart from saltpetre and kelp, nearly up to the middle of this century, *wood ashes* formed practically the only source of potassium compounds employed for technical purposes. Another important source of potassium salts is the ashes of *seaweeds*, called *kelp* in Scotland and *varec* in Normandy, which from times immemorial have been obtained by employing the seaweed as fuel; since 1811, when iodine was dicovered in these ashes, and a special industry had been founded thereon, those potassium salts have also been utilised. Somewhat later another vegetable source was opened out for potassium compounds—viz. the *vinasse*—that is, the residue left on distilling fermented beet-root molasses. Hence the expression 'vegetable alkali,' by which potash was distinguished from soda, when Duhamel, in 1736, had proved the separate existence of those bodies, was altogether appropriate, not only at this time, but even much later, until the Stassfurt discoveries made that designation altogether unsuitable.

Even the animal kingdom contributes a certain quantity of potassium compounds, in the shape of the carbonate of potash from the 'yolk' of *sheep's wool* (*suint*).

Interesting communications on the history of potashes are made by E. O. von Lippmann in Chem. Zeit. 1908, 977.

Metallic potassium. The compound nature of the alkalis, and the presence in them of oxygen, had been suspected previous to 1807 (*v.* Lavoisier, Traité de Chimie, II. 194), but the isolation of potassium was not effected until that year, when Davy obtained it by electrolysis of the fused hydroxide (Phil. Trans. 1808, 1; 1809, 39; and 1810, 16). The metal was soon prepared in larger quantity by Gay-Lussac and Thénard (Ann. Chim. Phys. 1808, 65, 325, and 1808, 66, 205) by slowly passing the hydroxide over iron filings heated to whiteness in a gun-barrel protected by a luting of clay, their process being modified by Berzelius (Gilbert's Annalen, 6, (N. F.) 198), Mantell (Annals of Philosophy, Thompson and Phillips, 22, 232), Gmelin (Handb. 3, 5), and Tennant (Annalen, 93, 291).

An important improvement was next introduced by Curandau (Ann. Chim. Phys. 1808, 66, 97, and Phil. Mag. 1810, 36, 283), who replaced the iron by carbon or carbonaceous matter. This, and the other processes in use, were examined by Brunner (Bibliothèque Universelle de Genève, 1823, 22, 36, and Schweigger's J. für Chem. und Phys. 35, 517), who also improved upon the apparatus employed by Bucholz (Ann. Chim. Phys. 73, 78), Trommsdorff (Gilbert's Annalen, 30, 333), Lampadius (Schweigger's J. für Chem. und Phys. 34, 221), and others.

Brunner's process as improved by Wöhler (Pogg. Ann. 1825, 4, 23, and 474), consists in carbonising potassium bitartrate in a covered vessel, and heating the resultant mixture of carbon and potassium carbonate with powdered charcoal in a mercury bottle, at the temperature of a powerful wind furnace. Kukla (Zeitsch. für Phys. und verwandte Wissenschaften, 1837, 5, 466), Werner (J. pr. Chem. 14, 267), Schœdler (Annalen, 20, 2), and Gale (Amer. J. Sci. 19, 205, and 21, 60), proposed various arrangements and lutes for protecting the retort from the furnace, the two first, and Pleischl (Zeitsch. für Phys. und verwandte Wissenschaften, 2, 307 and 343, 3, 326) also proposing modifications in the mixture used.

The method of condensing was next improved by Donny and Mareska (Ann. Chim. Phys. [iii.] 35, 147, *v.* also Mitscherlich, Lehrb. der Chem. 2, 10); while the addition of chalk to the mixture was found to facilitate the reduction by rendering the mass pasty instead of liquid at the reduction temperature, thus preventing the separation of the carbon from the alkali (*v.* Deville, De l'Aluminium (Paris, 1859), 650; and Kühnemann, J. 1864, 180).

For the preparation of potassium in a state of greater purity, Matthiessen (Chem. Soc. Trans. 1855, 8, 27) proposed the electrolysis of the easily fusible mixture of potassium and calcium chlorides.

The use of sodium instead of potassium for the manufacture of aluminium was introduced in 1854 by Deville (Ann. Chim. Phys. 1856, 46, 415), who also made improvements in the manufacture of the metal. Since then, sodium has almost entirely replaced potassium for use in the arts. The inconvenience and waste attending the manufacture of potassium, owing to the production of explosive compounds with carbon monoxide (*v.* Liebig, Annalen, 11, 182, and Brodie, Chem. Soc. Trans. 12, 269), accounted to some extent for its former high price. By Castner's electrolytic process potassium can be produced at a price not greatly exceeding that of sodium.

The various processes employed in the preparation of potassium are identical with those used in sodium manufacture, and are described, together with a list of patents and other matters relating equally to both metals, in the article SODIUM.

Potassium obtained by any process in which carbon monoxide is a constituent of the evolved gases, always contains the explosive compound above mentioned, which renders it liable to detonate on the slightest friction. For this reason, it must be redistilled, once or twice, when so prepared.

Properties.—Potassium, when freshly cut, has a brilliant, silvery metallic lustre. It crystallises in obtuse octahedra, showing a greenish-blue tint (Long, Chem. Soc. Trans. 1860, 13, 124).

According to Baumhauer (Ber. 6, 655), its sp.gr. at 13° is 0·875. At 0°, potassium is brittle, and possesses a crystalline fracture. At 15°, it acquires a waxy consistency and a few degrees higher becomes pasty, melting at 62·5° (Bunsen, J. 16, 178) and boiling at 719°–731° according to Carnelley and Carleton Williams (Chem. Soc. Trans. 1879, 565), or at 667° according to Perman (Chem. Soc. Trans. 1889, 328). The vapour has a green colour, and attacks glass and porcelain. Its characteristic channelled absorption spectrum has been examined by Roscoe and Schuster (Proc. Roy. Soc. 22, 362).

The lowering of the melting-point of potassium by the presence of sodium, gold, and thallium has been determined by Heycock and Neville (Chem. Soc. Trans. 1889, 666).

Potassium dissolves in liquefied anhydrous ammonia forming a deep-blue solution, from which the metal is re-obtained on evaporation of the ammonia (Seeley, Chem. News. 23, 169). It is the most electro-positive element known with the exceptions of cæsium and rubidium, and is an extremely powerful reducing agent. Hence the use of potassium for the preparation of less electro-positive elements, such as boron, silicon, magnesium, aluminium, &c., for the reduction of gases containing oxygen out of organic and other compounds.

On exposure to the air, it rapidly becomes converted into the hydroxide and finally into the carbonate. It decomposes water with sufficient energy to ignite the liberated hydrogen. Carbon dioxide passed over heated potassium is reduced to carbon, with formation of potassium oxide.

Potassium unites directly with the halogens and with sulphur, selenium, tellurium, and phosphorus, burning brilliantly when heated with them. When heated in carbon monoxide it forms a black mass identical with the explosive body produced in the manufacture of potassium.

Alloys. Potassium forms alloys with most metals, usually by being heated with them. The more important alloys are described under the various metals. With *sodium*, potassium forms alloys of low melting-point, as observed by Davy. Greville Williams (Chem. News. 3. 21) obtained an alloy melting below the ordinary temperature and containing about one-fourth its weight of potassium by heating sodium with potassium hydroxide to about 171°; whilst Wanklyn (Chem. News. 3, 66) has obtained a similar alloy by heating sodium with potassium acetate.

Potassium combines directly with *mercury*, with evolution of heat. The melting-points of a number of these amalgams have been determined by Merz and Weith (Ber. 14, 1445). When containing 70–96 parts of mercury to 1 part of potassium, the amalgam is crystalline. With 30 parts of mercury, it is hard and brittle. When heated to 440°, they all leave a crystalline amalgam of the composition HgK_2, spontaneously inflammable on exposure to air (De Souza, Ber. 9, 1050), but all the mercury is evolved below a red heat. Kraut and Popp (Annalen, 159, 188) have prepared a crystalline amalgam of the composition $Hg_{24}K_2$.

Potassium oxide, K_2O, is made by the Badische Anilin- und Sodafabrik (D. R. P. 143216) by heating potassium nitrate with metallic potassium, air being excluded: $KNO_3 + 5K = 3K_2O + N$. For the same purpose the nitrite KNO_2 may be employed, and in the same manner mixtures of K_2O and Na_2O may be obtained.

Potassium peroxide, K_2O_4, is industrially prepared by Jaubert (D. R. P. 189822) by heating, with special precautions, an alloy of potassium with lead, tin, or sodium at a moderate temperature in a current of air.

Potassium hydroxide *v. infra.*

Potassium chloride. This salt, which in commerce is generally known as '*muriate of potash*,' was formerly obtained as a by-product in various manufactures, such as the working up of kelp for iodine, from the spent lye of soapmakers, in refining native saltpetre, &c. The quantities thus obtained were not very large, if compared with the present state, and they were principally used in the manufacture of alum and of potassium chlorate. Some more potassium chloride was afterwards obtained in Balard's process of working-up the mother-liquors from the manufacture of sea-salt, and a good deal more in the manufacture of potashes from vinasse (*cf. Potassium carbonate, infra*).

But all this sinks into insignificance beside the enormous quantities obtained from the *Stassfurt carnallite*, and we shall therefore here describe the Stassfurt occurrence of potassium salts, as well as the methods of manufacture pursued here.[1]

The village of Stassfurt is situated on the river Bode, not far from Magdeburg, in Prussian Saxony, close to the borders of the small principality of Anhalt. In 1850 Stassfurt numbered 2000 inhabitants; in 1885, owing to the development of the carnallite industry, 16,000, and the adjoining newly-formed village of Leopoldshall (in Anhalt), 4000 inhabitants. The Stassfurt brine-springs are mentioned as far back as 1227, and in the last century 7,000 tons of salt per annum were made there in 30 salt-pans; but about 1815 the production of salt from brine was stopped there, having ceased to be remunerative in the face of competing brine-springs. In 1839 the Prussian mining office commenced boring for rock-salt, and in 1843 the salt was struck at a depth of 850 feet. The boring was continued for another 1080 feet without getting to the bottom of the stratum of salt; but the brine pumped up was extremely impure, containing, together with sodium chloride, a large quantity of magnesium chloride, potassium chloride, and magnesium sulphate. It was, however, conjectured at once that these salts might be deposited in separate strata, and it was resolved to sink two shafts. These were commenced in 1852, and within five years they had reached a thick stratum of pure rock-salt, after having penetrated a number of strata of other salts, of an aggregate thickness of 530 feet, which were called 'abraumsalze,' because they were at first considered useless, and had to be taken away before getting to the rock salt.

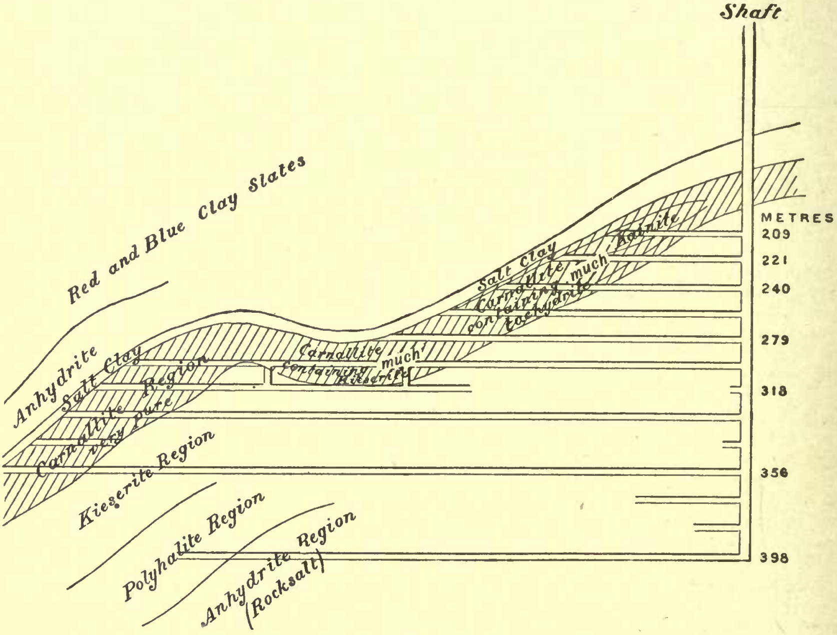


FIG. 1.

Later on it was found that the salt deposits occupy an enormous basin in the North German Plain, which has been successfully tapped in several other places, of which we mention only Sperenberg, near Berlin, where the boring was continued through the enormous thickness of 3940 feet of salt without getting to the bottom; also at Segeberg, near Lübeck, and in other places. But *potassium* salts in great quantity until quite recently had been found only in one locality, in the vicinity of Stassfurt, where the 'Abraumsalze' occur in the Upper New Red Sandstone. According to Chem. Zeit., Aug. 22, 1911, large deposits of sylvine have been discovered in Upper Alsace, in an area of about 200 square kilos., near Mülhausen. Two strata have been found, the upper one 3 feet thick, the lower one more than 16 feet thick estimated to contain some 1500 tons, but the borings will have to be deep, say 1600 to 2100 feet, which entails a very high temperature. This field, unlike the North German deposits, seems to be continuous, without faults. Geologically it is much more recent than the Stassfurt beds. But the recovery of potassium salts from the Alsatian field has not yet become a commercial fact, and we therefore confine our description to the Stassfurt deposit:—

In 1856 and 1857, the two Prussian shafts at Stassfurt; in 1861, the Anhalt shaft at Leopoldshall; in 1876, two shafts at Douglashall, near Westeregeln; in 1876, a shaft at Neu-Stassfurt; in 1878–1883, another two shafts at Stassfurt:

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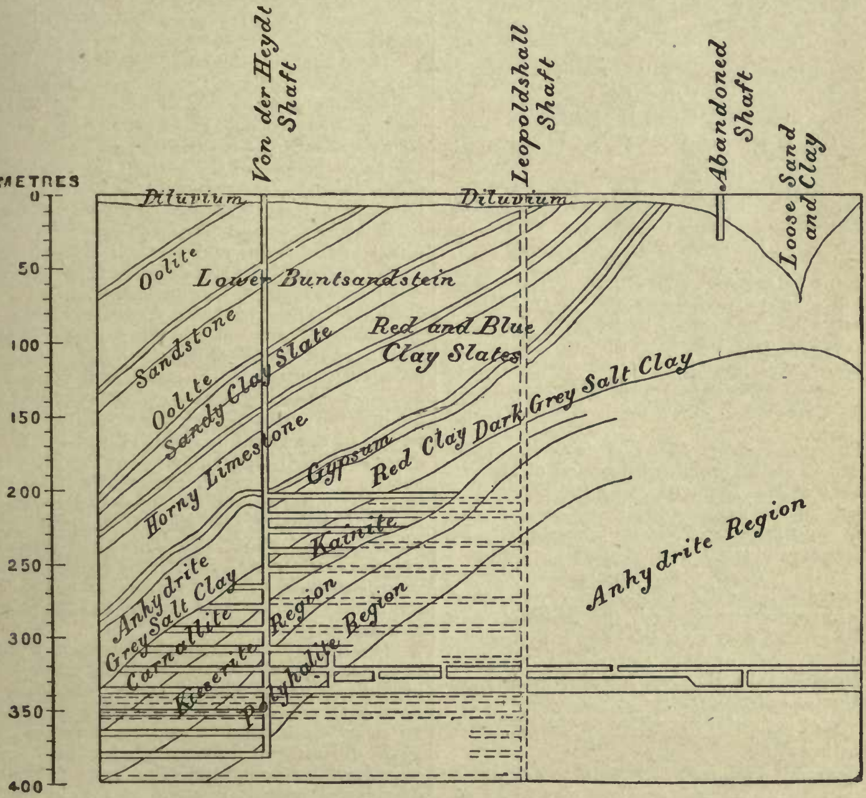
[1] In this part we follow to a great extent the detailed description by Pfeiffer, in his Handbuch der Kali-Industrie, Braunschweig, 1887 (*cf.* also, for some details, Hake, J. Soc. Chem. Ind. 1883, 146; and Borsche, J. Soc. Chem. Ind. 1888, 296; Kubierschky, Die Deutsche Kaliindustrie (1908); Krische, Die Verwertung des Kalis (1909); Ehrhardt, die Kaliindustrie (1907); Precht, die norddeutsche Kaliindustrie (1907)). A very important series of researches on the formation of the Stassfurt deposits has been made by van 't Hoff and his coadjutors, in 1897 and later on.

in 1883, a shaft at Aschersleben, sunk by the Continental Diamond Rock-Boring Company; some more shafts at Solvay's mines, near Bernburg, at Schönebeck, &c.; the Hercynia shaft at Vienenburg.

The profiles (Figs. 1 and 2) give an idea of the strata pierced in the two oldest and most important shafts at Stassfurt and Leopoldshall.

At Stassfurt itself the total thickness of the salt strata is estimated at about 2500 feet, and the time necessary for their formation at about 8000 years. F. Bischof, who has examined them most thoroughly, divides them into the four following 'regions,' of which only the first and the last have become of technical importance.

1. *Anhydrite or rock-salt region*, so called from the strings of anhydrous calcium sulphate which divide the rock-salt into bands of an average thickness of nearly 4 inches, each of which is supposed to be a year's growth. The layers of calcium sulphate are only ¼ inch thick, and amount only to 4 p.c. by weight of the rock-salt in the upper strata, or 9 p.c. in the lower strata.



METRES
0
50
100
150
200
250
300
350
400
Von der Heydt Shaft
Leopoldshall Shaft
Abandoned Shaft
Loose Sand and Clay
Diluvium
Diluvium
Oolite
Lower Buntsandstein
Sandstone
Red and Blue Clay Slates
Oolite
Sandy Clay Slate
Grey Salt Clay
Horny Limestone
Gypsum
Red Clay Dark
Kainite
Anhydrite Region
Anhydrite
Grey Salt Clay
Carnallite
Kieserite Region
Polyhalite Region

FIG. 2.

By mechanically separating the anhydrite, rock-salt of 99 p.c. NaCl can be obtained on a large scale. Small quantities of *hydroboracite*

$(CaMgB_6O_{11},6H_2O)$

and of a strontium sulphate are found here as well. The thickness of this stratum varies a great deal; in the centre of the basin it may be estimated at about 2000 feet.

2. *Polyhalite region.* Here the rock-salt is already mixed with mother-liquor salts, of which the dominant one is *polyhalite*

$2CaSO_4,MgSO_4,K_2SO_4,2H_2O$.

Magnesium chloride accompanies the rock-salt, and small quantities of sulphur and of bituminous substances are found here. The average composition of this stratum is: 91 rock-salt, 6⅔ polyhalite, ⅔ anhydrite, 1½ magnesium chloride; its thickness is 207 feet.

3. *Kieserite region*, so called from the occurrence of white bands of kieserite $MgSO_4,H_2O$. The average mixture is:

65	p.c.	rock-salt
17	,,	kieserite
13	,,	carnallite
3	,,	bischofite, $MgCl_2,6H_2O$
2	,,	anhydrite.

This stratum has a thickness of 187 feet.

4. *Carnallite region.* This contains 55 p.c. of *carnallite* $KCl,MgCl_2,6H_2O$, the most valuable of the Stassfurt salts, together with 25 p.c. rock-salt, 16 p.c. kieserite, the remaining 4 p.c. consisting of magnesium chloride (*bischofite*) $MgCl_2,6H_2O$, magnesium bromide $MgBr_2,6H_2O$, *tachydrite* $(CaCl_2,2MgCl_2,12H_2O)$, *boracite* or *stassfurtite* $(2Mg_3B_8O_{15})$, *anhydrite* $CaSO_4$, *reichhardtite* $(MgSO_4,7H_2O)$, clay, sand, micaceous oxide of iron, &c. The thickness of this stratum is 140 feet.

In some places the action of water has produced important changes in this region which have replaced the kieserite and part of the carnallite by *kainite* $K_2SO_4,MgSO_4,MgCl_2,6H_2O$; or $KCl,MgSO_4,3H_2O$, according to another way of grouping the constituents (about 55 p.c. of the whole), part of which has passed over into *schoenite* (*picromerite*) $K_2SO_4,MgSO_4,6H_2O$. In other places the magnesium chloride has been washed out entirely, and the mixture contains 20 p.c. of pure potassium chloride, *sylvine*, with 30 to 40 p.c. of rock-salt, and an equal quantity of kieserite and other impurities. Only exceptionally *astrakanite* $Na_2SO_4,MgSO_4,4H_2O$ is found.

Other Stassfurt minerals of minor importance are: *leonite* $K_2Mg(SO_4)_2,4H_2O$;
löweite $K_2Mg(SO_4)_2,2\frac{1}{2}H_2O$;
langbeinite $K_2Mg_2(SO_4)_3$; *glaserite* $K_3Na(SO_4)_2$; *vanthoffite* $Na_6Mg(SO_4)_4$;
krugite $K_2MgCa_4(SO_4)_3,2H_2O$;
pinnoite $MgB_2O_4\ 3H_2O$;
ascharite $Mg_6B_6O_{15},2H_2O$;
kaliborite or *heinzite* $KMg_2B_{11}O_{19},9H_2O$; *magnesium sulphoborite* $3MgSO_4,2Mg_3B_4O_4,12H_2O$.

The salts are covered by from 20 to 33 feet of *salt-clay*, over this from 133 to 300 feet of *anhydrite*, and this again by 80 to 100 feet of very pure, transparent *rock-salt*, free from calcium sulphate, evidently a secondary formation.

Formation of the Stassfurt deposits. There can be no doubt that the formation of the salt deposits of the North German Plain has been caused by the evaporation of sea-water. But there must have been special causes why, in a comparatively small part of that large area—viz. in the vicinity of Stassfurt—potassium and magnesium salts have been separated in large quantities, whilst on the greatest part of the ground only rock-salt and anhydrite are found.

According to Regnault, the average composition of sea-water is:

Total percentage of solids	3·53
consisting of:	
Sodium chloride	76·49
Potassium chloride	1·98
Magnesium chloride	10·20
Magnesium bromide	0·06
Magnesium sulphate	6·51
Calcium sulphate	3·97
Calcium bicarbonate	0·08
	99·29

We find here all the materials for the formation of the Stassfurt deposits, the average composition of which has been stated by Bischof, as follows:

	Percentage expressed in minerals
Rock-salt	85·1
Anhydrite	3·7
Polyhalite	0·8
Kieserite	3·3
Carnallite	6·2
Magnesium chloride	0·9

	Percentage expressed in salts
Sodium chloride	85·1
Potassium chloride	1·7
Potassium sulphate	0·2
Magnesium chloride	2·6
Magnesium sulphate	3·1
Calcium sulphate	4·0
Chemically-combined water	3·3

Since Bischof's time the bottom of the deposit has been reached, and it can now be said that the percentage of sodium chloride and of calcium sulphate is much higher than he assumed.

If we compare the composition of the Stassfurt deposits with the results of the artificial evaporation of sea-water as carried out in 1849 by Usiglio (Ann. Chim. Phys. [iii.] 27, 92), we find that there are some differences, partly caused by the long duration of the natural process and its yearly interruption, partly by the loss of mother-liquor (*v. infra*). The various salts were transformed into the minerals now present by a subsequent loss of water and by their mutual interaction, and a regular succession of those minerals was formed through long periods, caused by the autumnal influx of fresh sea-water. One remarkable difference also is this: whilst in artificial evaporation the calcium sulphate is entirely precipitated at an early stage, it is formed at Stassfurt even in the strata consisting of mother-liquor salts. Why the calcium sulphate at Stassfurt is in the form of anhydrite, not in that of gypsum ($CaSO_4,2H_2O$), as in the artificial evaporation of sea-water, we understand now from the observations of Hoppe-Seyler (Chem. Zentr. 1866, 217) and Rose (*ibid.* 1871, 613), according to which the hydration water of gypsum is abstracted from it by contact with a *nearly-saturated* solution of sodium chloride, a condition which we must assume to have existed at Stassfurt.

It is quite evident that the Stassfurt deposits have not been formed by the simple evaporation of a basin of normal sea-water, which would have been required to possess a depth of about 30 miles, and which would have produced a very different arrangement of salts. There must have been conditions similar to those even now found present in some of the Sarmatian lakes. Thus Göbel found at the bottom of Lake Elton a salt deposit of a thickness of 12 feet, consisting of 100 annual layers, which increased in strength and hardness from the top downwards, and at the bottom were as hard as stone. This lake is filled with a saturated brine; by the surface-evaporation in summer, crusts of common salt are formed, which sink to the bottom. Later on, the common salt gets mixed with Epsom salt and other mother-liquor salts, which form a porous, bitter, and deliquescent layer. The autumnal rains and floods partly dissolve and partly densify this top layer, and at the same time cover it with black mud, thus forming a distinct boundary line upon which the next year's crusts are formed again. In spring the water of that lake contains 15·5 p.c. sodium chloride and 10·5 p.c. of magnesium chloride; in autumn it holds but a small quantity of liquor containng only 4 p.c. NaCl, with 20 p.c. $MgCl_2$.

The nearest approach to the Stassfurt conditions is found in the Adji-Darja Bay, in the east of the Caspian Sea, a bay of a superficial, area of 2000 or 3000 sea miles, and almost entirely separated from the Caspian by a bar. There is, however, a small channel through which the water, abstracted by the intense evaporation within the bay, is replenished from the Caspian. This causes a continuous separation of salt, which is estimated by Schleiden at about 400,000 tons per diem, and the formation of a mother-liquor, part of which finds its way back into the Caspian. Where the depth of the bay is greater, the concentrated liquor sinks to the bottom, causing a state of sursaturation at this place and the deposition of mother-liquor salts. Without this, practically all the mother-liquor would flow back over the bar, and no mother-liquor salts would be formed; and this seems to have been the condition of most of the rock-salt, forming basins of former geological periods. In the case of the Stassfurt salts we must undoubtedly assume an *intermittent* influx of water, and also a number of geological elevations and depressions of level in order to account for the succession of the various strata. We may, with very great probability, assume the following play of causes: the Stassfurt basin was a valley, inclosed by two longitudinal folds of the earth's crust, communicating at one end with the ocean by a shallow bar, over which, in autumn, the gales and high tides carried large quantities of sea-water; not sufficient, however, to replace the water lost by evaporation. For a long period only gypsum was deposited here; afterwards common salt was formed as well, which converted the gypsum into anhydrite, but which for a long time was re-dissolved every autumn by the dilution of the liquor, caused by rain and floods. Thus the thick crust of gypsum and anhydrite was formed which lines the bottom of the basin. Later on, the liquor became more and more concentrated; the crusts of common salt now became permanent, and the yearly deposits increased in thickness. The sursaturation of the liquor at the bottom caused the transformation of the common salt into rock salt (as first proved by Mohr). Just as we observe it now in the 'salt gardens' on the Mediterranean, the last portions of the summer salt contained a little gypsum, but the greatest quantity of gypsum was precipitated when the strong brine came into contact with fresh sea-water breaking over the bar, thus forming a distinct line of separation against the next year's deposits in the shape of the 'anhydrite strings.' Since there was less and less room in the basin for fresh sea-water, those strings decreased in thickness during this period, which must have lasted several thousands of years, during the later part of which the yearly deposits had an average thickness of 3½ inches. Owing to further concentration of the liquor the crusts of salt in the later part of summer were more and more mixed with Epsom salt, which appears also with the gypsum precipitated soon after by the influx of fresh sea-water. In this period, which must have lasted 500 or 600 years, *polyhalite*, $K_2SO_4,MgSO_4,2CaSO_4.2H_2O$, was formed in the following way: some carnallite, $KCl,MgCl_2,6H_2O$, formed in summer, was at that period always decomposed in autumn by fresh sea-water, and the potassium chloride thus set free and coming into contact with the deposited Epsom salt was converted into potassium sulphate, which met with enough magnesium and calcium sulphates to form polyhalite. Exceptionally, indeed, carnallite is actually found in that region. During the next period of 500 years, with increasing concentration, some carnallite was regularly formed, but the principal deposit at that time consisted of *kieserite* $MgSO_4,H_2O$. It has been proved by Precht (Ber. 14, 2131) that from a concentrated solution of magnesium chloride, such as must have filled the basin at that period, the magnesium sulphate is separated by evaporation, not in the state of Epsom salts ($MgSO_4,7H_2O$), but in that of kieserite. This compound being insoluble, as well as the anhydrite, the formation of polyhalite was not any more possible.

During the fourth and last period of 500 years, when there was less room for the influx of fresh sea-water, the formation of *carnallite* got the upper hand. Pfeiffer has proved that that salt, and even hydrated magnesium chloride, can be made to crystallise by spontaneous evaporation at the temperature of hot summer days in our present climate. The formation of carnallite must have been still abundant, and a deep layer of mother liquor, in which magnesium chloride prevailed, must have been standing over the potash-bearing strata when new geological changes caused the eruption of a mighty mass of clayey mud, charged with organic substances, which sank to the ground, forming a layer of salt clay, 26 feet thick, which protected the underlying strata against a subsequent solution of the salts previously deposited, even after the mother-liquor had run off. The loss of that liquor accounts for the difference between the average composition of the Stassfurt deposits and that of the sea-water (comp. above). Wherever such accidental protection was not afforded, the surface-water must have re-dissolved the upper strata, which accounts for the general absence of mother-liquor salts in other localities.

Apart from Stassfurt, the following occurrences of potassium salts require mentioning:—

In 1866 at Kalusz, in Eastern Galicia, potassium salts were found in large quantities, principally consisting of sylvine and kainite, and a large manufacturing industry was commenced. But the quality of the salt proved inferior to the first samples, and in 1875 the works were discontinued, for various reasons, as being unable to compete with Stassfurt.

Small quantities of potassium salts, always of poor quality, have been found in the Punjab, in Persia, and in Colorado. None of these deposits gives any promise of industrial application.

The *rock-salt* in the mines round Stassfurt is not now obtained from the lower strata, where the admixture of anhydrite brings it down to 95 p.c., but from the upper (secondary) strata at Neu-Stassfurt, where it comes up to 99 p.c. of real sodium chloride. There is also a large quantity of pan-salt made in the neighbouring Schönebeck salt works.

The average composition of *crude carnallite* is:

	Per cent.
Potassium chloride	15·7
Sodium chloride	21·5
Magnesium chloride (with a little bromide)	21·3
Calcium chloride	0·3
Magnesium sulphate	13·0
Insoluble (anhydrite, clay, &c.)	2·0
Water	26·2

Small quantities of rubidium (0·001–0·003 molecules), cæsium and ammonium, and of bromine (0·005–0·01 mol.) are always present in carnallite.

It is sold on a basis of 16 p.c. potassium chloride; salts with less than 12 p.c. potassium chloride are hardly ever worked.

Crude kainite generally contains:

	Per cent.
Potassium sulphate	24·0
Magnesium sulphate	15·5
Magnesium chloride	13·0
Sodium chloride	31·0
Gypsum and clay	1·5
Water	14·0

Kainite is not very much worked now.

Hartsalz is a mixture of about 20 p.c. sylvine, 25 p.c. kieserite, and 55 p.c. rocksalt.

Sylvinite is the name given to crude kainite or hartsalz, if the percentage of potassium exceeds 13 p.c. K_2O.

Crude sylvine (not to be confounded with sylvinite) is a raw material of great importance, consisting of varying quantities of sylvine and rock-salt; the percentage of KCl varies from 25 to 50, sometimes even 80 or 90 p.c.

Crude kieserite is very impure, much more so than the residual product obtained in the manufacture of potassium chloride. Still, about 12,000 tons per annum are used.

Boracite, with 52 or 53 p.c. crystallised boracic acid, is obtained as a by-product.

The manufacture of Potassium Chloride at Stassfurt.

At first the importance of the strata found underlying the rock-salt at Stassfurt was not recognised, and it is principally due to the untiring exertions of Dr. A. Franck since 1860 that this was ultimately done. In 1861 he erected a small factory, and was immediately followed by Messrs. Vorster & Grüneberg, and soon after by Messrs. Leisler & Townsend. The last-mentioned factory—called the 'English factory'—which was designed on the principle of introducing as much mechanical labour as possible in lieu of manual labour, was very important for the later development of that industry. In 1864 there were already 18, in 1872, 33 different potash works at Stassfurt, in 1887 the number was 35.

The raw material for the manufacture is the crude carnallite as supplied by the mines in tolerably uniform quality; its average composition has been stated above. The principles of working it up are as follows: carnallite, $KCl,MgCl_2,6H_2O$, is unstable in the presence of water; it is decomposed into a magma of very finely crystallised potassium chloride and a solution of magnesium chloride, retaining but little KCl at a low temperature. On heating, the solution dissolves much more KCl, and on cooling the latter salt is separated in much larger crystals so long as the proportion of $MgCl_2$ does not exceed three times that of KCl. When that proportion has been reached the liquor on further concentration yields a crop of carnallite, which at a low temperature is very little soluble in the remaining solution of magnesium chloride. Of the foreign salts present in crude carnallite, rock-salt is much less soluble in hot $MgCl_2$ solution than KCl, and thus remains behind to a great extent; kieserite, which is insoluble as such but turns into soluble Epsom salts on heating with pure water, is prevented from so doing by the presence of magnesium chloride. The remaining substances are not of much consequence; some of them are quite insoluble.

Practically it has been found useful to treat the ground raw material, not with water, but with waste liquor from a previous operation in such quantity that it suffices for dissolving the carnallite present at a boiling heat; the solution is separated from the residue (the washings being utilised for a fresh solution) and is allowed to cool down, when it deposits about 80 p.c. of the potassium chloride; the mother-liquor, on further evaporation and cooling, yields the whole of the remaining KCl as a crop of carnallite which is decomposed by water as above. The products are purified in the manner described below.

The first operation, *dissolving the crude carnallite*, is the most important of all for the success of the manufacture. The result differs very much according to the quality of the crude carnallite, according to its state of division, according whether pure water or liquors obtained in other stages of the manufacture are employed, and also according to the duration of the operation. It is, in principle, preferable to effect the solution of carnallite as quickly as possible in order to dissolve less of the other salts. The quickest operation is undoubtedly that practised at the 'English' factory—crushing the crude carnallite into powder, and dissolving it in a close vessel at several atmospheres pressure with mechanical agitation. But this process causes too much rock-salt and even kieserite to be dissolved at the same time, and it also causes the formation of very much mud; hence most manufacturers work at the ordinary atmospheric pressure, or very little above it, without mechanical agitation, and employ coarsely-crushed carnallite.

Fig. 3 shows one of the usual descriptions of dissolver. The true bottom *g* is slanting, the false bottom *e* is horizontal. The latter is perforated by a large number of holes ⅓-inch wide; in the centre there is a double-hinged trap-door *b*, also perforated. The two halves of this door are suspended from the hinged arm *a*; they are closed when *a* is in the upright position, in which it is kept by the vertical rod *h*. When the liquor has been run off through *c*, the man-hole *f* is opened and the rod *h* is knocked away, which causes the arm *a* to turn over, and the two halves of *b* fall down. The residue is now easily washed down from *e*, and cleared out through *f* by a strong jet of water passed all over *e* by means of a hose. The steam-pipe *d*, with two rows of holes, is carried round the central opening of *e*. The conical shape of the bottom has the two-fold advantage that the liquor can be run off completely and that the residue can be got out very quickly.

Formerly the dissolvers were made of wrought iron, but since it has been recognised that cast-iron resists much better the chemical action of the salts, it has become usual to employ cast-iron cylinders, with a conical bottom, provided with a sieve, below which the steam is introduced, the head of the steam-pipe being closed by a bulb with many perforations.

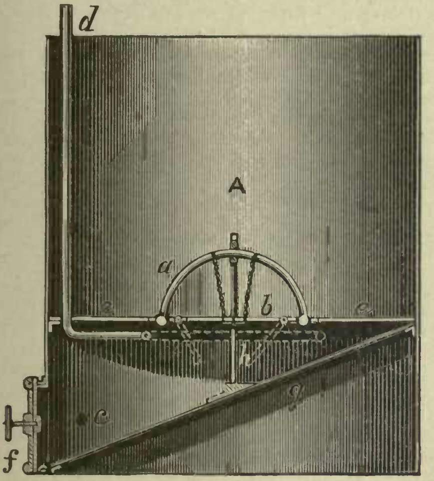


Fig. 3.

Where it is considered desirable to dissolve under a slight pressure, the top of the dissolver is covered in, the man-hole being closed during the work, or else a tube reaches down from the cover into the liquid, nearly to the false bottom, in order to introduce the salt, and to produce some degree of steam pressure in the apparatus. The waste steam can be employed for heating up the dissolving-liquor in another pan. Such vessels, of a capacity of about 350 cubic feet, admit of working up 50 tons of salt and more in 24 hours.

The liquor employed for dissolving (called 'Löselauge') is a mixture of various liquors resulting in the manufacture, especially the washings of the first residue, and those of the potassium chloride, as well as various mother-liquors, altogether of a sp.gr. 1·268 to 1·279; through being heated up by waste steam, the liquor comes down to 1·257, and is used in this state. This liquor is run into the dissolver until this is half full; steam is injected until the liquor is brought to boil, and only then the crude carnallite is introduced. For each 100 cubic feet of tank room, from 30 to 36, or at most 42 cwt. of carnallite can be charged. The solution is first brought to sp.gr. 1·313 to 1·337 (measured hot and in the muddy state), but in this state the residue would be very difficult to treat; there would be considerable loss of potassium chloride by crystallising out before the liquor was clarified, and the potassium chloride obtained in the coolers would be contaminated by newly-formed carnallite. To avoid this, the solution is diluted to sp.gr. 1·28 or 1·30 (measured hot and muddy). The operation of dissolving ought not to last more than half an hour, or, including other necessary work, 2 hours, so that 12 operations can be made in 24 hours.

The solution must now be clarified by allowing it to rest for an hour or two in settling-vessels, and drawing off the clear portion by means of a drop-siphon. The clarifying operation can be promoted by sprinkling a little milk of lime on the surface, which precipitates some magnesia, the latter carrying down the other impurities. The residue must be once or twice boiled up with fresh water, if the crude carnallite had been employed in lumps of the size of a fist; if, as now usual, it had been more finely crushed, it is either removed at once, or it is previously boiled up with a small quantity of mother-liquor, the resulting liquor being utilised as part of the dissolving liquor for fresh carnallite, or by cooling down, when it yields weak potassium chloride.

The following analyses show the composition of the ultimate residue, forming from 26 to 30 parts of the crude carnallite:

	a	*b*	*c*
Potassium chloride .	5·25	3·0	2·2
Sodium chloride .	47·00	45·0	54·8
Magnesium chloride	3·85	2·0	2·5
Magnesium sulphate	29·25	38·0	22·9
Calcium sulphate .	2·15	0·7	1·8
Insoluble . .	6·00	5·3	5·0
Combined water .	6·50	6·0	10·8
	100·00	100·0	100·0

a is a product as formerly obtained, *b* and *c* more recent products of different works. The 'insoluble' is mostly anhydrous calcium sulphate, clay, boracite, and sand.

The residue was formerly allowed to accumulate in large heaps, part of which only was utilised for manufacturing kieserite and sodium sulphates; where there was not room enough for depositing it, it had to be washed away by a stream of water. Recently, it is largely employed for filling up the old workings in the carnallite mines, since this has been required by Government regulations in order to prevent subsidences of the soil.

A different kind of residue is obtained by thoroughly settling the liquid in tanks, protected against cooling, and drawing off the clear liquor by means of a drop-siphon. This second residue, the 'kieserite mud,' consists essentially of kieserite, accompanied by a little anhydrite, clay, boracite, gypsum, sodium chloride, &c.; also by potassium chloride. It is separated from the liquor by means of a vacuum filter, or, preferably, of a filter-press in which it can also be washed by hot mother-liquor, which removes the potassium chloride without affecting the other salts to a great extent. Even then from 4 to 26 p.c. of potassium, calculated as chloride, are retained in the mud, probably in the shape of potassium magnesium sulphate.

Formerly the clear liquor was purposely allowed to cool down to some extent, say to a temperature of 80° or even less, before being run into the crystallising vessels, in order to precipitate some sodium chloride. But since the solution is now made by means of mother-liquors, the clear liquor contains less NaCl, and is generally at once employed for crystallisation. The following analyses refer, I. to a liquor made with water, of sp.gr. 1·3 (at 105°) in the muddy, and 1·284 in the clarified, state; II. to a liquor made with mother-liquor, of sp.gr. 1·313 (at 105°) before being diluted with water; III. shows the maximum and minimum percentages found in ordinary liquors:

	I.	II.	III.
Potassium chloride .	11·08	10·70	8–14
Sodium chloride .	5·68	4·20	4–8
Magnesium chloride .	17·65	24·60	15–25
Magnesium sulphate .	2·92	1·50	1·5–5
Water	62·67	59·00	—
1 cubic metre contained . . .	142·2	140·5 kilo. potassium chloride.	

The crystallising vessels (coolers) are wrought-iron tanks of various sizes, usually from 150 to 300 cubic feet capacity—*e.g.* 7×8×4 feet, with bottoms slanting a little to one side, where there is a plug for running off the mother-liquor. They are best placed a little above the floor, so that the air can circulate underneath, and in summer this should be promoted by Venetian shutters in the building. If the cooling takes place too quickly, the crystals are too small and muddy. Two or three days ought to suffice.

The salt first precipitating carries down such suspended matters as had not been removed by settling; hence such 'bottom salts' are less pure than the 'side salts' crystallising afterwards. The quantity of the latter is sometimes increased by suspending bundles of wire in the coolers, but this is now done but rarely, as the extra labour is hardly recompensed by the advantages of that process. When the cooling has been finished, the mother-liquor is siphoned off, or is run off by a plug, exactly as in the manufacture of soda crystals.

The proportion of bottom salts to side salts ranges from 2 down to 1 part of the former to 1 of the latter; some analyses of this 'first product' run as follows:—

——	Bottom salts		Side salts		Mixtures of both
	Drained	Dry	Drained	Dry	
Potassium chloride	50·2	59·76	60·8	58·31	64–69
Sodium chloride .	27·0	32·14	24·4	27·42	28–22
Magnesium chloride	4·3	5·12	2·8	3·15	7·5–8·5
,, sulphate	2·0	2·38	1·0	1·12	0·5–0·5
Insoluble . .	0·5	0·60	—	—	—
Water . .	16·0	—	11·0	—	—

The mother-liquor drained off from the crystals of KCl retains about $\frac{1}{5}$ of the total KCl, most of which is recoverable by evaporation and cooling the concentrated liquor.

The following are analyses of the 'first mother-liquor,' as remaining behind from the 'first product' (I. former process, II. present process):

	I.	II.
Specific gravity at 20°	1·273	1·279
Potassium chloride .	5·50	4·50 p.c.
Sodium chloride. .	3·80	3·20 ,,
Magnesium chloride .	19·90	22·80 ,,
Magnesium sulphate .	2·70	2·15 ,,
Water . . .	68·10	67·35 ,,

Part of it is employed for dissolving fresh crude salts as mentioned above; the remainder is concentrated by evaporation until nearly all the KCl can be obtained on cooling as artificial carnallite. This concentration was formerly carried out in two stages—first to sp.gr. 1·279 (when low-grade potassium chloride was obtained), and then to 1·325; but now, since coal is dearer and lower prices are obtained for the product, it is found best to concentrate at once to 1·325, which means evaporating about one-third of the bulk of the liquor, till the boiling-point reaches 123°.

The evaporation must be carried on in such manner that the heating surfaces are not covered by crusts of salts, and, of course, in such a way that the fuel is utilised in the best possible manner. Evaporating by means of steam-coils has been found less economical than by means of open fires. Passing over the antiquated modes of concentration as formerly employed at Stassfurt, we shall describe the more recent process. It is now usual to carry on the evaporation successively in two different kinds of apparatus—namely, first, up to the point where salts would be separated in the boiling liquor in ordinary two-flued steam boilers, the steam being utilised for dissolving and other purposes. In lieu of this the first stage is now usually, and with very great advantage, carried on in combinations of vacuum-pans, such as have been in use for a long time in sugar works, and here and there for caustic liquor. The second stage of concentration, where salts are separated during the process, is best carried on in open pans, heated by internal flues, as shown on a scale of $\frac{1}{75}$ in Figs. 4 and 5, which at the same time illustrate the 'step-grates,' universally employed at Stassfurt for the friable brown coal found in the neighbourhood. The flame, generated on the grate *g*, passes through the central wrought-iron tube *a* and back again through the lateral tubes *bb* into the brick flues *ll*. The very strong boiling of the liquor prevents the formation of any crusts of salts on the tubes *a* and *b*.

It has now become general to cover in these pans, and to utilize the steam escaping from them in various ways. The consumption of fuel (lignite) has been greatly diminished by the introduction of gas-producers.

The first stage of evaporation, that in which no salts are separated, ends a little above sp.gr. 1·26; during this time the evaporation is continuous, fresh liquor being run into the boiler to keep it up to the same level. In the second stage the salts were formerly removed by fishing, which might be done more advantageously by mechanical means. It is, however, usual to boil down to sp.gr. 1·32 or 1·33 in winter, 1·33 or 1·345 in summer (testing the liquor in the muddy and hot state), to allow it an hour's settling, and to run it then into a cooler. The fished salts and the settling mud are washed with water, the washings being utilised for dissolving crude salts; but even then they contain from 7 to 12 p.c. potassium, calculated as chloride, together with 50 to 66 p.c. of sodium chloride, and cause an appreciable loss, as it is not easy to extract that potassium chloride with advantage.

The clear liquor contains about 5·5 to 6 KCl, 2–3·3 NaCl, 25–29 $MgCl_2$, 2·6–3 $MgSO_4$, and 59–64 H_2O. It is run into coolers, and left there during three or four days. At first—that is, down to a temperature of 65°—principally sodium chloride crystallises out, and this can be kept out by a previous cooling down to that temperature. On further cooling, 'artificial carnallite' is separated, usually containing from 18 to 22 p.c. KCl, equal to 67–82 p.c. of real carnallite, together with a little NaCl, $MgCl_2$, and $MgSO_4$. This salt is dissolved in water, brought to boiling heat by means of open steam, till the sp.gr.=1·268 (at 105°) has been attained, and a little milk of lime is added at the finish, in order to remove any iron present and to mechanically clear the liquid. The dissolving and settling last an hour each, the subsequent cooling three or four days. Sometimes the 'artificial carnallite' is decomposed in the cold way, by agitating it with cold water until most of the $MgCl_2$ is dissolved, and separating this solution by suction from the solid KCl remaining behind. The result of the operation is solid potassium chloride, 'second product,' and a 'second mother-liquor,' of sp.gr. 1·257 (measured cold), with 3–4 p.c. KCl, which is usually added to the first mother-liquor in the concentrating pans.

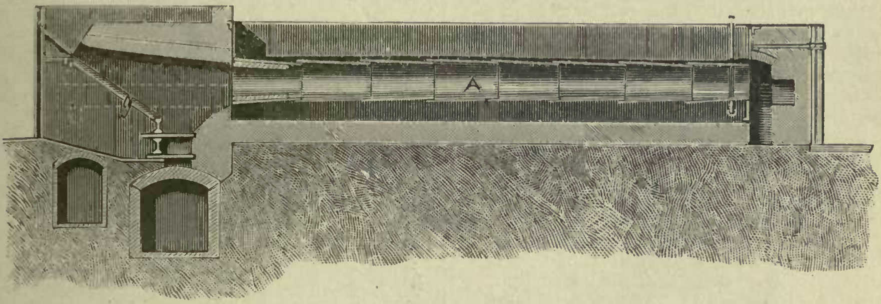


Fig. 4.

The quantity of second product amounts to about 20 p.c. of the total make of potassium chloride; its analyses show its comparative purity:

Bottom salts.

	Drained	Dry
Potassium chloride .	67·0	77·38
Sodium chloride .	13·7	15·82
Magnesium chloride .	5·3	6·11
Magnesium sulphate .	0·6	0·69
Water . . .	13·4	—

Side salts.

	Drained	Dry
Potassium chloride .	80·2	89·02
Sodium chloride .	7·0	7·77
Magnesium chloride .	2·6	2·88
Magnesium sulphate .	0·3	0·33
Water . . .	9·9	—

The following are tests of the 'final mother-liquor'—*i.e* that which remains after the crystallisation of the artificial carnallite:

	Former process	Present process
Specific gravity . .	1·319	1·313
Potassium chloride .	1·25	1·20
Sodium chloride . .	0·95	1·20
Magnesium choride . .	29·50	28·05
Magnesium bromide .	0·30	0·31
Magnesium sulphate .	2·22	3·10
Water	55·78	66·14

Its quantity is 5 or 7 cubic metres to each 10 tons of crude carnallite, and it is now usually worked for *bromine* (*q.v.*); partly also for magnesium chloride (*v. infra*).

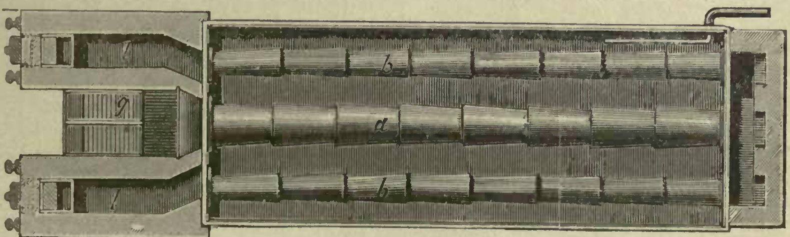


Fig. 5.

Purification of potassium chloride. This is always performed by washing, utilising the fact that at low temperatures the solubility of KCl decreases very much more than that of NaCl, $MgCl_2$, &c., and that the contact of water with those salts itself causes a lowering of the temperature (sometimes amounting to 10°), so that the water in winter would be turned into ice if it were not employed in the tepid state.

The washing of the salt takes place in iron vessels, provided with a false bottom, upon which the salt rests. This false bottom is made of wood or of iron plates, perforated with ⅜-in. holes, and is covered with sacking, or, preferably, with a web of split cane. The water or liquor employed for washing is sprinkled upon the salt by means of an elastic tube, ending in a rose, and the liquor is removed from underneath the false bottom by means of a tap or plug. In Fig. 6, A is the tub, *a* a man-hole through which the washed salt is removed at the end, *b* the false bottom, *c* the tube and rose for washing, *d* the charging bogie, *e* the running-off tap.

The tub is completely filled with salt, and this is first washed with washing-liquor from a former operation, which in this way yields some of the KCl previously taken up, and takes up NaCl in this stead. After having twice served in this way, the liquor is used for dissolving crude carnallite, in the first operation described above. The first liquor is run off at once, until the mother-liquor has been displaced; the tap *e* is now closed, fresh liquor is run on to the top of the salt, leaving it in contact with the same for two hours, and then running it off. This is repeated with once-used liquor, and last of all with fresh water. The washing-tubs are best suspended from the staging by means of trunnions, with toothed-wheels for turning them on their axis at the end of the operation, for the purpose of emptying out the washed potassium chloride.

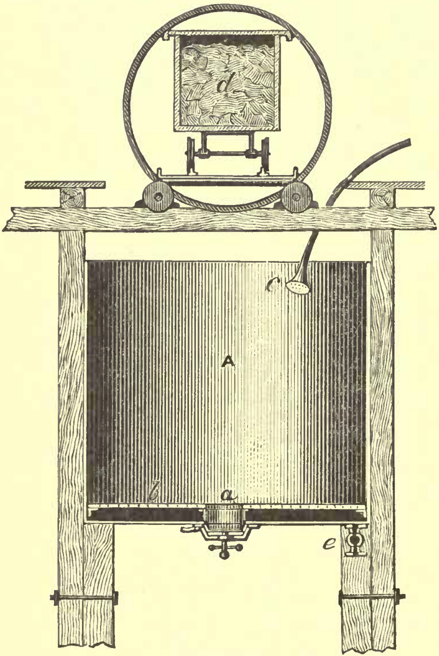


FIG. 6.

The washing operation is not advantageous with products containing less than 50 p.c. KCl; such products are better purified by re-crystallisation.

The washed salt naturally contains a considerable quantity of water. By simple draining this can be got rid of down to 7 or 9 p.c., by centrifuging to 5 p.c. The remainder is removed by heating, which was formerly mostly done in reverberatory furnaces. The apparatus in general use now is shown in Fig. 7 on a scale of $\frac{1}{50}$. Upon the foundation *i* a cast-iron drum *h* is mounted, the hollow part of which is heated by steam through *m*, whilst at *n* there is a steam-trap for the removal of the condensed water. In the centre there is a perpendicular shaft, *l* revolving in a bearing protected by a cap. This shaft is moved by means of the pulleys *u* and the bevel wheels *k*, and it carries the horizontal arm *t*, to which are attached a number of plough-shares *a*, a crushing-roll *b*, and a discharging-scraper *c*, set in motion by handle *e* and lever *s*. The last-mentioned part serves at the end of the drying operation for moving the salt towards the circumference, where it falls through an opening, kept shut up to this time by a slide, into a shoot and bag attached to it. Each charge yields 60 kilos. dry salt, and each drying-plate turns out from 2 to 2½ tons per day of 27 hours. With wrought-iron plates of 8 feet diameter, which transmit the heat more easily, nearly 5 tons can be dried in 24 hours. In some places Thelen's mechanical drying-pans are employed, which are heated by direct fire, and yield about 15 tons per 27 hours, with an expenditure of 8 to 10 p.c. of brown coal (the fuel value of which is not quite one-half that of ordinary coal).

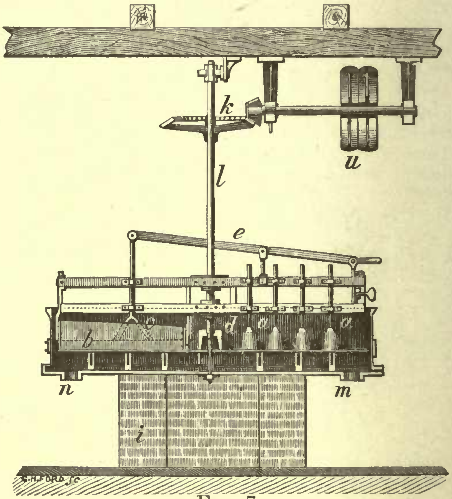


FIG. 7.

Whichever apparatus may be employed, the formation of crusts cannot be entirely avoided. These are removed once a day, and are crushed in order to be sold as manure salts, containing about 70 p.c. KCl.

The drying is usually carried up to 2 p.c. water for low grades, or 0·5 p.c. for high grades; but it is best to leave the salt a short time in a cool, dry place before packing. It is then crushed between rolls, sifted, and packed into jute bags, holding 100 kilos. each.

ANALYSES OF COMMERCIAL POTASSIUM CHLORIDE.

—	*a*	*b*	*c*	*d*	*e*	*f*
KCl .	80·85	89·78	82·00	96·5	84·30	98·58
NaCl .	16·25	8·10	16·00	2·0	12·98	0·22
$MgCl_2$	0·20	0·10	0·40	0·2	0·19	0·07
$MgSO_4$	0·59	0·33	0·30	0·2	0·10	0·12
$CaSO_4$	0·18	0·27	0·25	0·3	0·22	0·24
Insol. .	0·33	0·32	0·15	0·2	0·23	0·31
Water	1·60	1·10	0·90	0·6	1·98	0·46

a and *b* manufactured in 1869, *c* and *d* in 1873, *e* and *f* in 1884.

Another process for treating carnallite has been patented by Schliephacke and Riemann (D. R. P. 43932). They smelt raw carnallite in a cupola furnace with felspar or granite, and run the liquid product into cold water, whereby it is granulated and the soluble salts are more easily extracted. Magnesium silicate remains behind in an insoluble state; the solution, which contains the potassium as silicate, is treated with a solution of crude carnallite or waste liquors from the manufacture of potassium chloride. The ensuing reacton is:

$$MgCl_2+K_2SiO_3=MgSiO_2+2KCl,$$

so that only potassium chloride remains in solution. The gases escaping from the throat of the cupola furnace are to be treated for chlorine and hydrochloric acid. (This ingenious process does not seem to have been practically carried out.)

Manufacture of potassium chloride from sylvine.—This is an exceedingly simple matter, since a hot saturated solution of $KCl+NaCl$ on cooling allows nothing but KCl to crystallise out. Ground sylvine is dissolved in the same way as described in the case of carnallite; the solution, if necessary, is cleared by subsidence and allowed to crystallise, just as the solutions obtained from carnallite. The resulting potassium chloride tests 92–94 p.c. KCl, even without washing, and by washing can be brought up to 98 p.c. Experience has shown that the crude sylvine should not contain more than ¾ p.c. MgO (in the shape of kieserite); if it contains more, both MgO and SO_3 are removed by adding milk of lime. A modified process for obtaining sylvine from mixtures with rocksalt, &c., is described in the D. R. P. 132474 of Speyerer.

The manufacture of KCl from *hartsalz* is carried on in a similar manner, *e.g.* by Tünger's D. R. P. 102075; but as this material is of very varying composition, the special rules for working must be fixed from case to case.

Meyerhoffer (D. R. P. 91906) obtains potassium chloride from carnallite by heating this to about 167°. About three-quarters of the KCl is thus obtained in a solid form, whilst the remainder and all the $MgCl_2$ remains in solution which, on cooling down to about 115°, deposits nearly all the KCl and leaves only $MgCl_2$ in solution. The same inventor (D. R. P. 92812) purifies carnallite by heating to about 265° and removing the fused carnallite by presses from the residue. Further improvements are described in his D. R. PP. 98344, 99957, 109101.

The Salzbergwerk Neustassfurt (D. R. P. 138562) dissolves the carnallite *in situ* underground by means of tepid water, the solution being pumped up.

Maurer (D. R. P. 166558) gives detailed prescriptions for the preparation of potassium chloride from the crude Stassfurt salts.

Haag and Glienicke (D. R. P. 163413) fuse the carnallite out of the crude salts by electric heating.

BY-PRODUCTS OF THE STASSFURT POTASH INDUSTRY.

1. Kieserite. This insoluble body,

$$MgSO_4,H_2O,$$

which becomes soluble only by prolonged contact with water, when it passes over by an intermediate stage into Epsom salts $MgSO_4,7H_2O$, is naturally left behind in the residues from dissolving crude carnallite and settling the liquor. Most of it is lost in the shape of pit heaps, &c.; only then is it regularly recovered by the potash manufactures, when they are obliged to get rid of their residues by washing away, because in this case the law compels them to retain the insoluble portions; otherwise kieserite is only prepared when there is special demand for it. Since it soon passes over into the above-mentioned intermediate stage, it must be made from fresh residues, which is done by subjecting them to a combined levigating and sifting process. A convenient apparatus for this purpose is shown on a scale of $\frac{1}{50}$ in Fig. 8, where *g* is a hopper containing the residues, which rest on a grating; the water issuing from *b* produces a muddy liquor, which meets the slanting sieve *c*; the coarser portions run off at *f*, the finer ones pass through into the slanting shoot *d*, where at first anhydrite is deposited, whilst further on, at *e*, kieserite is found. The clay, together with a little boracite, remains suspended till the last, and is kept back in special settling basins. Of course, in lieu of the slanting shoot *d*, several settling troughs with overflows can be employed.

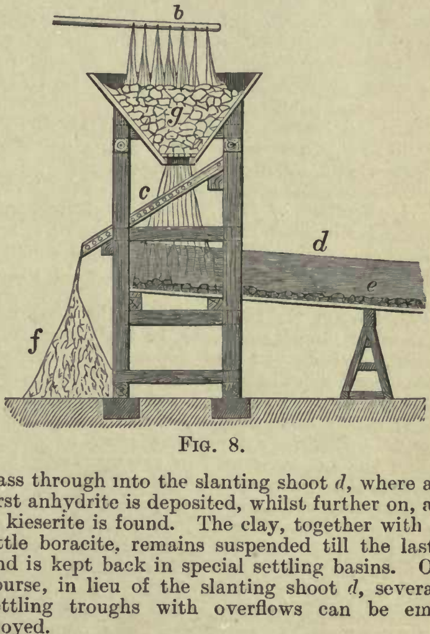


Fig. 8.

The kieserite must be removed at short intervals and put into iron or wooden moulds, where it solidifies after fifteen minutes, so far that the blocks can be taken out. The solidification (which is a process similar to that occurring with gypsum, a chemical combination with water taking place) proceeds with evolution of heat; in a few days the blocks, weighing ¼ to ½ cwt., are as hard as stone, and can be sent out in this state without being packed in casks, bags, or the like. After a lapse of time, however, they fall to powder by the attraction of atmospheric moisture and formation of Epsom salts.

The quality of block kieserite naturally varies, according to the more or less careful separation from other matters; a minimum of 55 p.c. magnesium sulphate is frequently guaranteed. When it is required in the ground state, it is first calcined in a reverberatory furnace.

ANALYSES OF KIESERITE BLOCKS.

—	Fresh		Calcined	
	a	b	a	b
Magnesium sulphate	60·20	58·0	81·5	77·8
Sodium chloride	1·55	2·1	2·1	2·7
Insoluble (anhydrite, &c.)	10·63	13.5	14·4	17·0
Water	27·62	26.4	2·0	2·5

The yield of block kieserite is about 10 p.c· of the crude carnallite. With careful work it can be got up to 12 p.c., but this is scarcely ever done, because at present only one-tenth of the residues is worked for it, the demand not being equal to the supply.

A small quantity of block kieserite is converted into *calcined kieserite*, with a guaranteed minimum percentage of 70 p.c. $MgSO_4$, by calcining in ordinary reverberatory furnaces, grinding and packing in bags.

The Gewerbschaft Carlsfund (D. R. P. 166187) obtains kieserite from its mixture with common salt by digestion with more or less concentrated salt solutions.

Applications of kieserite. Most of it is employed for making Epsom salts, some of it for potassium sulphate. We mention the following attempts at utilising the substance in other ways.

G. Clemm (in 1863) calcined the kieserite, preferably mixed with coal, in the presence of steam, and carried the vapours into vitrol-chambers; magnesia remains behind (in a very impure state). By a similar process Precht (in 1881) makes basic linings for the steel process. Several other inventors have tried to utilise either the sulphuric acid or the magnesia, but hitherto not to any appreciable extent.

The only extensive employment of kieserite is that of converting it into *Epsom salts*, of which about 25,000 tons per annum are made in Germany, and a considerable quantity in England and in the United States. The process consists simply in causing the kieserite to take up more water, preparing a solution, and allowing this to crystallise. Formerly the process was promoted by calcining the kieserite, after which it is at once soluble in water; but this object can be equally attained by the prolonged application of steam, or, even more cheaply, by soaking the crushed kieserite with the mother-liquor from the Epsom salts, when it gradually passes over into the heptahydrated salt, with great increase of bulk. A solution is now prepared by water and steam, of sp.gr. 1·31 to 1·325 (tested hot and muddy). This is clarified in settlers, where it is kept about an hour; the last particles of gypsum and clay, floating in the liquor, are removed by wood-lined filter-presses; the purified solution (if necessary concentrated in lead-lined pans by means of lead coils) is run into lead-lined iron or wooden crystallising vessels.

After three or four days the crystallisation is finished; the crystals are all the finer the more concentrated the liquor had been, and they are at first practically free from sodium chloride. By concentrating the mother-liquor inferior qualities are obtained; the last liquor is run to waste.

The crystals of Epsom salts are in England merely drained by a centrifugal machine, turning out 2 tons per day, and the product, still containing 3 or 5 p.c. of moisture, is directly packed into casks; in Germany they are dried in a room heated by exhaust steam, &c., at a temperature not exceeding 45°, the dry salt is passed through wooden rollers, leaving a space of $\frac{3}{8}$ inch, so that only the lumps are crushed; it then passes through a sieve, and from this into the casks.

The favourite shape of Epsom salts is that of fine needles, of silk-like lustre, which are most easily formed by moderately quick cooling of a concentrated solution. The coarser crystals are separated by sifting and re-dissolved, or sold as second quality.

The principal application of Epsom salts was formerly the medicinal one, which, of course, did not amount to large quantities. At present the greater portion of it is employed in finishing textile fabrics, especially calico. Other applications (mostly only proposed or temporarily tried) are those for replacing the 'pearl-hardening' in paper-making (mixed with lime), for preparing precipitated barium sulphate, for purifying beet-root sugar juice, for rendering fabrics fire-proof, for manufacturing sulphur trioxide, in several soda-making processes, and so forth.

2. **Glauber's salt** $Na_2SO_4,10H_2O$, can be made by Balard's process—that is, exposing a mixed solution of sodium chloride and magnesium sulphate to a temperature below 0°, when the following reaction takes place:

$$2NaCl+MgSO_4+10H_2O=MgCl_2+Na_2SO_4,10H_2O.$$

The Glauber's salt crystallises out, magnesium chloride remaining in solution. At the mouth of the Rhone this is done by artificial cold; at Stassfurt it can be done without that during the winter months. The material is present in the residues from dissolving crude carnallite, the composition of which has been stated on page 342. Just the weathered residue which is no more adapted for the treatment for kieserite, is most suitable for the above process, and from 50,000 to 75,000 tons of Glauber's salt might thus be made per annum; but the quantity actually produced is only about 10,000 tons, and varies very much according to the nature of the season.

The residue is dissolved in various ways; the longer it has been exposed to the weather, the more easily the solution takes place. Usually the residue heaps are lixiviated on the spot by means of hot water, the solution being caught in a trench made at the bottom of the heap. If the proportion is not $=2NaCl$ to $1MgSO_4$, the composition of the liquor is corrected and its strength is brought up to about 1·269 at 33°. The solution is clarified by settling, and is exposed to the cold of a winter's night, always under the open sky. Ordinary coolers are not so well adapted to this purpose as large, shallow tanks, made of pine-wood planks, the joints being made tight by caulking with hemp and tar. These tanks are erected on wooden pillars, and are sometimes 100 by 100 feet square, and 8 inches deep. During summer, when they are not used, they are kept filled with a solution of common salt. In such shallow tanks the liquor is better cooled down during the night, 1 cubic metre often yielding 150 to 180 kilos. of crystals. The mother-liquor is run off in the early morning, before it can get warm again; it shows the sp.gr. 1·205 to 1·225.

3. **Magnesium chloride** $MgCl_2,6H_2O$, is obtained by evaporating the 'final mother-liquor' in the same description of apparatus as described above for the treatment of carnallite liquors, usually in pans with flame-pipes, to a b.p. of 157° which corresponds to sp.gr. 1·388 or 1·40 (taken hot), allowing to settle for an hour, and running into a cooler, whereupon the whole mass solidifies in a few days. It is broken into large pieces, which are put into casks; the empty space is filled up by a hot, strong solution of magnesium chloride, which on cooling, cements the whole into a solid mass. Sometimes the dry salt is melted for some time in a furnace, to expel some more water, but if this is driven too far, hydrochloric acid escapes as well. This process is much dearer than the first, and there is not much gained by it. A colourless, glassy product is obtained by boiling down only to sp.gr. 1·44, oxidising the ferrous salts by adding potassium chlorate (of which about 3 kilos. is required for a charge of 40 cubic metres of concentrated solution), heating further until a b.p. of 157° has been reached, and precipitating the iron by the addition of an excess of milk of lime (of which about 130 kilos. CaO will be required for 40 cubic metres of liquor), and cooling down to about 125°. The liquid is then run through the bunghole into petroleum casks, in which it solidifies, and is sent out in this state. The analyses show:

	Boiled down to sp.gr. 1·388	Boiled down to sp.gr. 1·44
Magnesium chloride .	45·74	51·05
Potassium chloride .	1·35	1·38
Sodium chloride .	0·25	0·27
Magnesium sulphate .	0·15	0·10
Water . . .	52·51	47·20

Since one ton of the product can be obtained from three (or, with care, from 2½) tons of crude carnallite, enormous quantities might be made at Stassfurt; but actually only about 12,000 to 16,000 tons are made, and are principally employed for dressing (lubricating) the warp in weaving calico. A very large number of further applications have been proposed, in order to utilise either the chlorine, or the magnesia, or both. We mention here the following applications: as a disinfectant; for precipitating waste soap-lyes; for carbonising wool; for making patent fuel; for magnesia cement; for preparing magnesia, principally as 'basic lining' in the manufacture of steel; for manufacturing barium chloride.

Crystallised magnesium chloride is made by evaporating only to sp.gr. 1·42 and pouring the liquor into casks, already containing blocks of $MgCl_2$ crystals, between which it solidifies. The crystal cakes contain about 43·0 p.c. $MgCl_2$, 1·3 KCl, 1·2 NaCl, 3·4 $MgSO_4$, 51·1 H_2O.

Magnesia and hydrochloric acid is made from magnesium chloride by two firms by means of secret processes. Probably the $MgCl_2$ is first converted into oxychloride, and this is then heated by gases containing a large quantity of steam.

Magnesia alone is made from magnesium chloride liquor by means of lime, in two stages, viz. first, precipitating the sulphuric acid and iron, if necessary with addition of a little bleaching powder and removing the precipitate; second, adding more lime to decompose the $MgCl_2$ into MgO and $CaCl_2$.

4. **Bromine** is largely made from the final mother-liquor of the Stassfurt works, which contains about 0·25 or 0·29 p.c. of it in the state of $MgBr_2$; *cf.* the article BROMINE.

Part of the $MgBr_2$ is converted into the iron compound Fe_3Br_8 and sent out in this state to the bromine works, or into the bromides of potassium, sodium, and ammonium.

5. **Boracic acid** is made from boracite or stassfurtite, $2Mg_3B_8O_{15},MgCl_2$, of which about 300 tons per annum is obtained at Stassfurt. It is dissolved in concentrated hot hydrochloric acid; the clarified solution is run into wooden coolers, lined with lead, where boric acid crystallises out. The crude acid is purified by washing or recrystalling. 100 parts of commercial boracite yield about 82 to 85 parts of crystallised boracic acid H_3BO_3, which is partly sold as such, and partly converted into the sodium salt, known in trade as borax (*q.v.*).

6. **Potassic manures** (*artificial fertilisers*) are made from all the by-products of the Stassfurt manufacturers, as well as from minerals specially got for this purpose, especially kainite. The manufacturing operations consist merely in grinding, drying, calcining, and effecting a proper mixture to bring the product up to the guaranteed percentage of potash. Potassium sulphate is much better for this purpose than chloride, and magnesium chloride in the free state is absolutely injurious to vegetable life. Hence kainite and schoenite (*cf. Potassium sulphate*) are most usually employed as manures; but low-grade potassium chloride is also frequently sold for this purpose (*v.* FERTILISERS).

Potassium chloride from the mother-liquors of the manufacture of sea-salt. The utilisation of the mother-liquors, obtained in the manufacture of sea-salt by voluntary evaporation in the 'salt gardens,' is not generally attempted. It has, however, been worked out to great perfection in at least one locality, at Giraud-en-Camargue, at the mouth of the Rhone, originally by Balard, later on by Merle and Pechiney. Descriptions of this industry have been given by Wurtz (Hofmann's Bericht über die Wiener Ausstellung, 1875, [1] 410) and Lunge (Chemische Industrie, 1883, 225). We quote here only those portions referring specially to potassium chloride.

From each cubic mètre of sea-water, after obtaining the salt, 64 litres of mother-liquor, testing 27°Bé., remains behind. This mother-liquor is concentrated by solar heat to 32½°Bé.; the salt crystallising out during this operation is of inferior quality (down to 91 p.c. NaCl), and is not utilised at all at Giraud. But on further evaporating, by solar heat, from 32·5° to 35°Bé., a mixture of sodium chloride with nearly its equivalent of magnesium sulphate is separated, which is known as 'sels mixtes,' and is worked up in various ways, especially for Glauber's salts, by artificial cold (p. 348). The liquor of 35°Bé. is kept during the winter in very large and deep tanks, where the temperature is prevented from falling below 12°C.; in this case only Epsom salt crystallises out, but no carnallite. The new mother-liquor, testing 33°Bé., of which 16 litres per cubic metre of sea-water has remained, is further evaporated by artificial heat in a Porion's furnace until it shows 37°Bé., tested hot. On the other hand, magnesium chloride solution, obtained at a later stage as a by-product, is evaporated in ordinary open pans to 40°Bé. Both hot liquors are run at the same time into an iron mixing-pan, taking care to maintain an excess of magnesium chloride. This causes at once a considerable separation of 'sels mixtes' (*cf.* above), which are removed by a dredging apparatus. The hot liquor remaining behind still contains all the potassium salt; this is, however, separated on cooling in the form of artificial carnallite, owing to the presence of so much magnesium chloride, most of which is left in the cooled-down mother-liquor. This artificial carnallite, being in the state of fine mud, is easily decomposed by agitation with cold water, when magnesium chloride enters into solution and potassium chloride is left behind in the solid state. By systematic washing the latter can be brought up to 82 p.c. KCl.

Interesting and ingenious as this process is (in reality it is much more complicated than would appear from the preceding short description), it cannot very well compete with the Stassfurt industry, based as this is upon the natural accumulation of similar products through thousands of years. Hence Balard's process has not made its way elsewhere, and is not likely to do so.

Potassium chloride from kelp. In the manufacture of iodine from kelp—that is, the ashes of sea-weed—as obtained on the coasts of Scotland and Normandy, a large quantity of potassium salts is obtained, which, previously to the working of the Stassfurt deposits, was one of the principal sources of these salts for technical purposes. The liquor obtained by lixiviating the kelp is concentrated by evaporation in several stages, and thus yields several crops of crystals. The first crop, called 'plate sulphate,' is a mixture of potassium sulphate with some sodium sulphate and common salt; the mother-liquor yields, on further evaporation while hot, a mixture of common salt with alkaline sulphates and carbonates, which is fished out from the pans and sold as 'kelp salt'; on cooling, a crop of potassium chloride is obtained. The latter can be brought up to upwards of 90 p.c., and formerly about 2500 or 3000 tons of it was made per annum; but the development of the Stassfurt industry has mostly compelled the iodine manufacturers to give up the separation of the potassium salts in the pure state, and to utilise the rough mixture of those salts for agricultural purposes.

Potassium chloride from beet-root vinasse. This product, which always contains potassium sulphate and foreign salts, is described further on, under *Potash from beet-root vinasse.*

Potassium bromide KBr can be made in various ways, always starting from the bromine, obtained in America, in Scotland, or at Stassfurt. Only two of these processes have come into practical use.

The first consists in dissolving bromine in a solution of potassium hydroxide, which ought to be as pure as possible, evaporating the solution, ultimately with addition of a little charcoal, and igniting the mixture. At first the reaction is as follows: $6KOH+6Br=5KBr+KBrO_3+3H_2O$. On igniting, the charcoal reduces the bromate to bromide. The mass is dissolved in water, filtered, and the potassium bromide obtained by evaporation and crystallisation.

This process suffers from the drawback that the mass decrepitates strongly on drying, and further losses through volatilisation, &c., cannot be avoided. Hence another process is almost exclusively employed now, similar to that used for potassium iodide. An iron bromide is first prepared, and this is decomposed by potassium carbonate. Some iron bromide is obtained in the manufacture of bromine, the vapours being absorbed by metallic iron, but most of it is made by mixing bromine and iron in such proportions that the compound Fe_3Br_8 is obtained (*cf. Potassium iodide*). The solution of this bromide is filtered, and is run into a hot concentrated solution of potassium carbonate, until the reaction is exactly neutral or very faintly alkaline. 100 parts of iron bromide require from 56 to 60 parts of potassium carbonate, according to its purity. The solution is boiled for some time, to make the precipitate of hydrated iron oxides more dense; it is then separated from the latter by a filter or filter press, and is evaporated to dryness. The residue is dissolved again, leaving behind the difficultly soluble potassium sulphate, &c., and is evaporated for crystallisation. Up to sp.gr. 1·53 this can be done at a boiling heat; the further evaporation should be done at a gentle heat, as with the iodide, to obtain hard crystals. The crystallisation takes place in stoneware or enamelled iron dishes. The mother-liquor can be freed from carbonate by cautious neutralisation with hydrobromic acid, and from sulphate by means of barium bromide. Any chloride present cannot very well be removed from the bromide; hence the bromine employed should be as free from chlorine as is required. Iodide can be removed by boiling with bromine. The last mother-liquors are best used up for the recovery of bromine. The German Pharmacopœia permits the presence of 2 p.c. KCl and 0·1 p.c. K_2CO_3 in potassium bromide.

The drying of the potassium bromide takes place at 40° or 50°C., not above (to avoid decrepitation), on plates of stoneware or of sheet-iron covered with a very hard lacquer or with enamel.

The German manufacture of potassium bromide amounts to about 120 tons per annum, half of which is made at Schering's works at Berlin. A similar or larger quantity is made in America, and much more could be obtained if there were demand for it.

The application of potassium bromide is restricted to medicine and photography.

Potassium iodide KI. There are many ways for preparing this salt, but only the following processes are used for manufacturing purposes.

1. *By means of potassium hydroxide.* The reaction is, $6KOH+6I=5KI+KIO_3+3H_2O$. The potassium iodate on igniting yields up its oxygen and is converted into iodide, but as losses are caused by decrepitation and volatilisation, it is preferred to add some carbon in order to reduce the iodate.

The potassium hydroxide ought to be as pure as possible; most of the impurities of the commercial product would enter into the iodide, and could not be removed from it by crystallisation, owing to the great solubility of the iodide. Hence it is preferable to start with the purest procurable potassium carbonate such as is supplied in the crystallised form to flint-glass makers, or that made by calcining potassium bicarbonate. The carbonate is causticised in the usual manner, employing pure lime, and iodine is introduced in small quantities into the boiling liquor until it has been exactly neutralised. The solution is evaporated to dryness, adding to it in the syrupy state some lampblack or charcoal, previously treated with hydrochloric acid and thoroughly washed with water, to the amount of $\frac{1}{20}$ of the iodine present. The dry mass is gradually introduced into an iron pot, heated to redness, where it is brought to fusion, keeping the pot covered in order to prevent the iodide from volatilising. When completely fused, the mass is ladled out and is dissolved in water; the solution is filtered and is evaporated to about 1·82, when it crystallises on cooling. The evaporation is best performed by heating the solution in porcelain dishes on a sandbath, but not to boiling heat, the more concentrated liquors being farthest from the fire-end. A hood protects each dish from dust, draught, &c. In this way very good crystals are obtained.

The crystals, after draining, are dried on enamelled or lacquered iron plates in a current of hot air. If the salt is required to have an opaque appearance, the temperature is ultimately raised to 120° or 130°C.

2. *By means of iron.* A solution of ferrous iodide is prepared by digesting 3 parts of iodine with 1 part of iron borings and about 8 of water. The solution is filtered and one-third of the original quantity of iodine is dissolved in it with the aid of heat, so that it now contains a ferroso-ferric iodide, Fe_3I_8. This solution is now mixed in a porcelain or enamelled iron vessel with a boiling solution of pure potassium carbonate, and the boiling is continued until the precipitate of ferroso-ferric oxide has become dense, whereupon it is separated from the solution of potassium iodide by filtration. The reaction is:

$$Fe_3I_8+4K_2CO_3=8KI+Fe_3O_4+4CO_2.$$

The following modification, by Liebig, dispenses with the slow solution of iodine in ferrous iodide, and the troublesome frothing in the last reaction, owing to the escape of carbon dioxide. A solution is made of 12 parts iodine, 3 iron, and 32 water; to this is added, without previous filtration, a solution of 6 parts iodine in 12 parts caustic potash liquor of sp.gr. 1·345, and ultimately 9 parts of the same caustic liquor. The mixture is boiled for some time, filtered, evaporated to dryness, whereby a little ferric hydroxide is separated, re-dissolved, filtered and brought to crystallisation as above. The product is extremely pure, free from iodate, and the yield almost theoretical.

3. *By means of cuprous iodide.* Sometimes considerable quantities of cuprous iodide, containing from 60 to 66 p.c. of iodine, are shipped from Peru. This is converted into potassium iodide by washing it, suspending it in water acidified with a little sulphuric acid, passing in sulphuretted hydrogen until all the copper has been precipitated, adding enough solution of iodine in potassium iodide to destroy the excess of H_2S, separating the solution of hydriodic acid (containing a little finely-divided sulphur) from the precipitate, neutralising it with potassium bicarbonate, evaporating, separating the sulphur which has now become globular, and bringing to crystallisation.

Nearly all the potassium iodide manufactured is employed in medicine and for photographical purposes. For the former purpose it is required to be entirely free from chloride.

Potassium sulphate K_2SO_4 is obtained as a by-product in several manufactures which are described elsewhere; thus, in the working up of beet-root vinasse (*cf. Potassium carbonate*, p. 358), and in that of kelp, where it is separated as 'plate sulphate,' containing from 76–83 p.c. K_2SO_4, with 9–21 p.c. Na_2SO_4, some KCl and other salts (p. 350). It is also contained in the ashes of plants, and hence is present in commercial potashes; on purifying these it is obtained as a by-product, easily separable from the carbonate on account of the great difference in solubility.

The bulk of the potassium sulphate found in trade is, however, made either from kainite, or by the decomposition of potassium chloride with sulphuric acid.

Very large quantities of potassium sulphate are found at Stassfurt and Kalusz; not, however, in the isolated form, but principally in that of *kainite* $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, always mixed with sodium chloride, calcium sulphate, &c., so that commercial kainite contains at most 70 p.c. of the pure mineral. A very large number of processes have been invented for preparing potassium sulphate, either from kainite or from mixtures of magnesium sulphate (in the shape of kieserite) and potassium chloride or carnallite. In most cases an intermediate product is made, the magnesium-potassium sulphate, $K_2SO_4,MgSO_4,6H_2O$, which occasionally occurs among the Stassfurt minerals, and has received the name of 'kalimagnesia' or 'artificial schoenite.' From this potassium sulphate is prepared with comparative facility, but at present it hardly pays to do so, at least in a sufficiently pure state for the manufacture of potassium carbonate; hence nearly all the latter is made from sulphate, obtained, with potassium chloride and sulphuric acid (*v. infra*), or from vinasse, while the schoenite is sold as a fertiliser.

We give here a short synopsis of the more important processes, which are described in detail in Pfeiffer's Kali-Industrie (Braunschweig, 1887), p. 349 *et seq.* The figures put in brackets are the numbers of the German patents.

1. *Preparation of artificial schoenite (kalimagnesia) from kainite.* Borsche and Brünjes (D. R. PP. 10642, 11028, 10701, 12875, 17795) prepare a cold saturated solution of kainite and employ this for extracting fresh kainite at a temperature of 80°. The solution, which shows the sp.gr. 1·337, is clarified, and on cooling yields a crop of schoenite; the mother-liquors, which are rich in magnesium and sodium and potassium chloride, generally enter into the manufacture of potassium chloride from carnallite. This process is actually at work on a large scale.

Dupré and Hake (D. R. P. 6053) treat finely-ground kainite with a cold saturated solution of magnesium sulphate, at 20° or 25°C.; this carries away magnesium and sodium chloride, together with one-third of the potash, two-thirds of the latter remaining behind as schoenite. The dissolved 33 p.c. of potash is also partially recovered. This process is also at work, but not on a very large scale; the employment of magnesium sulphate makes it rather more expensive than the preceding one.

H. and R. Grüneberg (D. R. PP. 10754, 18947) extract the kainite by a hot solution of schoenite or of sodium chloride; on cooling schoenite crystallises out.

Precht (D. R. PP. 10637, 13421, 19456) treats kainite with water or previous liquors at 120°–145°, under a steam-pressure of 2–7 atmospheres, with mechanical stirring, in a very ingeniously-constructed apparatus, which permits a mechanical separation of the double salt formed from the solution and from the residual rock-salt. The double salt formed in this way has the formula $K_2SO_4,2MgSO_4,H_2O$, and is converted into schoenite by agitation with a small quantity of water. This process is also at work on a large scale.

Similar processes are those of Loefasz (D. R. P. 29223) and Nahnsen (D. R. PP. 10772, 24744).

Dupré (D. R. P. 53237) works up mixtures of kainite and sylvinite ($75KCl+25NaCl$) by treating them with a hot solution of kainite, when almost pure $K_2SO_4,MgSO_4,6H_2O$ crystallises out. The same inventor (D. R. P. 68572) passes ammonia gas into a solution of kainite, separates the precipitated $Mg(OH)_2$, and again treats with ammonia, whereupon the whole of the potassium, in the case of pure kainite, crystallises out as K_2SO_4, or, if NaCl is present, as pure potassium-sodium sulphate, $K_3Na(SO_4)_2$. The ammonia is recovered from the last liquor by treating it with the magnesia, previously obtained.

The Westeregeln Alkali Works (D. R. P. 50596) boil ground kainite with the last mother-liquor from the manufacture of potassium chloride. containing 30 p.c. $MgCl_2$, thus producing various salts.

The schoenite thus obtained, which is entirely used for agricultural purposes, has the following average composition:

Potassium sulphate	48–52 p.c.
Magnesium sulphate	32–36 ,,
Water	3–12 ,,
Sodium chloride	1–5 ,,
Gypsum and insoluble matter .	0·2–5 ,,

Several processes for preparing schoenite from potassium chloride or carnallite and kieserite (Brünjes, D. R. P. 11; Ferber, D. R. P. 5068; Grüneberg, D. R. P. 5607; Westeregeln, D. R. P. 27404) need not be described here, because they do not seem to be profitable. The principal reaction taking place is

$$2MgSO_4+2KCl=K_2SO_4,MgSO_4+MgCl_2;$$

or better

$$4MgSO_4+6KCl=2K_2SO_4,MgSO_4+2KCl,MgCl_2.$$

Special processes for recovering schoenite from waste liquors are those of R. Grüneberg (D. R. P. 10753), Bernhardi (D. R. PP. 10821, 12493), Vorster and Grüneberg (D. R. P. 28772).

It is now a fixed rule of trade that 'crystallised' potassium-magnesium sulphate is to contain 41 or 42 p.c. and 'calcined,' 48 or 50 p.c. real potassium sulphate.

2. Kubierschky (D. R. P. appl. K. 29803) makes use of the fact that a solution of magnesium sulphate (kieserite), when appropriately diluted by water or KCl solution, on addition of solid KCl, at a temperature of 25°, does not yield schoenite, but at once a precipitate of potassium sulphate.

Saeger (D. R. P. 196500) describes a process for obtaining potassium sulphate from the mother-liquors of the manufacture of potassium chloride.

3. *Preparation of potassium sulphate from schoenite.* This can be done by simply running a saturated hot solution of schoenite upon dry powdered potassium chloride. The reaction theoretically is:—

$$K_2SO_4,MgSO_4+3KCl=2K_2SO_4+KCl,MgCl_2,$$

but practically twice the theoretical quantity of schoenite must be taken, half of which remains in solution. The potassium chloride is rapidly changed into sulphate, and this is separated from the liquor by centrifugal force, taking care that the temperature does not fall below 40°. Below this temperature, first potassium chloride, then schoenite, and at last carnallite, crystallise out. The reaction can also be brought about by digesting crystallised schoenite with a cold saturated solution of potassium chloride, best of all in a set of vessels methodically combined with one another (Precht, D. R. P. 14534).

Schoenite, or a mixture of potassium chloride and magnesium sulphate, can also be converted into potassium sulphate by heat. Superheated steam (Sprenger, D. R. P. 27965) acts only very partially, but the addition of carbon (in the shape of small coal, brown coal, &c.) causes the reaction to proceed to its end by somewhat complicated stages (Precht, D. R. P. 15747; Leopoldshaller Fabriken, D. R. P. 31148). Townsend (D. R. PP. 10641, 29307) heats a mixture of potassium chloride, magnesium sulphate, and aluminium silicate in a muffle furnace in the presence of steam. This method has been further worked out by the Ascherslebener Werk, in 1885, and seems to be successful. Hans Müller ignites the mixture of KCl and $MgSO_4$ with ferric oxide (D. R. P. 32325). Dupré and Hake produce, by means of lime or gypsum, a double sulphate of potassium and calcium, which is decomposed by igniting or by redissolving (D. R. P. 8021).

Nearly all the potassium sulphate made from schoenite, &c., is used for agricultural purposes.

In all processes for manufacturing potassium-magnesium sulphate (schoenite) or potassium sulphate, a great deal of trouble is caused by the large quantity of mother-liquor and the loss of potassium chloride from that cause. When this mother-liquor is boiled down, various salts are obtained which must be utilised as best possible, usually in the shape of fertilisers. *Rubidium alum* is also obtained from such mother-liquors.

4. *Preparation of potassium sulphate by decomposing potassium chloride with sulphuric acid.* This process, altogether analogous to the first stage of the Leblanc soda process, was first carried out by Messrs. Vorster and Grüneberg in 1863, near Cologne, and in 1868 at Stassfurt. About the same time (1864–1869) it was introduced in North Germany, France, and England. This way of producing potassium sulphate is nearly always employed when the product has to be converted into carbonate.

The raw materials are (1) potassium chloride of high strength of the Stassfurt manufacture, or, as far as it goes, that from the working up of vinasse which already contains from 8 to 12 p.c. of sulphate, together with a little carbonate (p. 358). Coarse-grained salt is preferred to muddy or lumpy salt. (2) Sulphuric acid of sp.gr. 1·67, generally made at the same works. This is a lower strength than that preferred for decomposing sodium chloride, where the reaction is not so violent.

The decomposition of potassium chloride is so closely akin to that of sodium chloride that we can refer in most respects to the article Sodium salts. The furnaces, acid-condensers, &c., are the same in both cases. We must, however, make the following remarks concerning some peculiarities of the potash industry.

The 'decomposing pans' (pots) are exactly similar to those used for common salt, so are the furnaces, of which all three descriptions, as employed for common salt, are in use here as well. But whilst in the case of sodium chloride the 'close,' or muffle furnaces are considered the best, owing to the better condensation of hydrochloric acid, many potash manufacturers prefer 'open'—that is, reverberatory—furnaces, a higher temperature being required for decomposing potassium sulphate and the work being done much more quickly (by one-third). Undoubtedly the best furnace for this work is Mactear's continuous revolving furnace as used at Kalk near Cologne.

The ordinary decomposing pans, which in England produce from 1500 to 2000 tons of salt cake before they are worn out, serve only for half or two-thirds that quantity with potassium chloride. At Stassfurt they employ thin pans, 2½ ins. thick throughout, which last only for 250–500 tons of potassium sulphate. Blügel's firebrick pans (D. R. P. 4207) do not seem to have answered.

The charges are from 5 to 10 cwt. of potassium chloride, and the corresponding quantity of sulphuric acid, which must be varied according to the varying strength of the chloride. The chloride coming from the vinasse works contains carbonate, which must be taken in account. With muffle furnaces the work is considered sufficiently good if 1 to 2 p.c. KCl and 2 to 3 p.c. 'free' SO_3 is left in the sulphate. Each charge takes about an hour to finish.

With reverberatory furnaces the undecomposed KCl is only 0·5 to 1·5 p.c.; the 'free' SO_3 1 to 2 p.c.

With Mactear's furnace the Kalk works produce from 22½ to 25 tons of potassium sulphate in 24 hours; the product contains only 0·7 to 1·0 p.c. KCl, and as much free SO_3 (that is, bisulphate). The condensation of the hydrochloric acid is very good, 95 p.c. of the theoretical quantity being recovered.

Theoretically 100 parts K_2SO_4 require 85·6 of pure KCl (corresponding to a yield of 116·8 of the former from 100 KCl), and 45·91 of SO_3= 75·27 acid of sp.gr. 1·67; and the HCl escaping should be 41·84 parts =138 parts hydrochloric acid of 32½ p.c. Practically with hand-furnaces 3·5 to 5 p.c., with mechanical furnaces 1 p.c., excess of sulphuric acid must be taken, or even more, if a minimum of undecomposed KCl has to be guaranteed.

The yield of sulphate is almost equal to theory, the small unavoidable loss being made up by matter mechanically taken up from the furnace, flue-dust, &c. The quality has been mentioned above.

The following is an analysis of good commercial sulphate made from 98 p.c. potassium chloride:

K_2SO_4 .	95·00 p.c.	SO_4H_2 . .	1·84 p.c.
Na_2SO_4 .	0·50 „	CaO,Al_2O_3,Fe_2O_3	0·81 „
KCl .	1·50 „	Insoluble . .	0·35 „

The yield of hydrochloric acid is usually only 70–75 p.c. of the theoretical one with reverberatory furnaces, 90 p.c. and upwards with muffle furnaces or the Jones and Walsh furnace, 95 p.c. with Mactear's continuous furnace.

The wages per ton of sulphate are from 6·5 to 7·2 marks (including the condensation of hydrochloric acid) for hand furnaces, but only one-half or even less for Mactear's furnace.

The fuel used amounts to 9 cwt. of good Westphalian coal with muffle furnaces, or 4–5 cwt. coke and 3 cwt. coal for reverberatory furnaces. With Mactear furnaces there is no saving of fuel, since it is necessary to provide steam for the engine turning the furnace.

Potassium aluminium sulphate (*Potash alum*) (*cf.* Alum).

Potassium carbonate. Impure potassium carbonate, commercial 'pot-ashes,' has been known from very ancient times. Aristotle mentions its preparation by the incineration of rushes, Dioscorides by that of argol. Kunkel, in the seventeenth century of our era, proved the identity of these two products. The Romans employed them in medicine and for soap-making; the latter is even now the most important outlet for that article, as soft soap cannot be made with soda. Otherwise soda tends more and more to displace the more expensive potash, and has done so in the manufacture of hard soap, in that of glass (partially even in that of flint glass and Bohemian crystal), and more recently, to some extent, even in some manufactures which formerly seemed to be only possible with the use of potash, as that of chromates, chlorates, and ferrocyanides. In the manufacture of oxalic acid from sawdust caustic potash is also considered indispensable.

Leaving aside such methods as cannot be classed among manufacturing processes (such as the incineration of argol or wine-lees) with or without potassium nitrate, we may enumerate the following commercial sources of potassium carbonate:—

1. *Mineral.* (*a*) From potassium chloride and sulphate by Leblanc's or other processes.

(*b*) From felspar and other rocks containing potash.

2. *Vegetable.* (*a*) From wood ashes.

(*b*) From beet-root molasses (vinasse).

(*c*) From kelp or varec (very unimportant).

3. *Animal.* From the 'suint' of sheep's wool.

Potassium carbonate (or caustic potash) manufactured from the chloride or sulphate. All processes starting from this base are of very recent date, and only that imitating the Leblanc soda process has acquired great importance. In 1861 Messrs. Vorster and Grüneberg, of Kalk, near Cologne, commenced working up potassium sulphate (which at that period was a by-product in working up vinasse cinder, less valuable than chloride, and difficult to get rid of) by the Leblanc process, and this industry has gradually spread over other parts of Germany, which is the principal seat of that industry. In England the Leblanc process seems to have been attempted with potash about 1863 or 1864, but it was only somewhat later employed for making commercial carbonate, and has not gained any great extension there. In France it was introduced in 1873, at Croix, near Lille, and at other works in the North.

We shall now enumerate the principal processes for manufacturing potassium carbonate from chloride or sulphate, omitting those which have been originally proposed for soda without special adaptation to potash.

(1) *From chloride, without passing through sulphate.* The *ammonia* process, which is of such importance for the manufacture of soda, is not applicable to potash, because the solubility of potassium bicarbonate is too great. An attempt to overcome this by working in an alcoholic solution, by Grousilliers (D. R. P. 10552), was entirely unsuccessful.

A very ingenious process is that of Ortlieb (D. R. PP. 5706, 9376, 13397), replacing ammonia by *trimethylamine*, which is obtained by a certain treatment of beet-root vinasse (*cf.* below). The great solubility of trimethylamine hydrochloride admits of separating the potassium bicarbonate; cold, pressure and agitation promote this object. The reaction is:—

$$KCl+N(CH_3)_3+CO_2+H_2O$$
$$=KHCO_3+N(CH_3)_3,HCl.$$

The limited supply of the reagent, its high price, its extremely unpleasant smell, are drawbacks to this process, which otherwise seems to have worked well in the experimental factory at Croix, where it was, however, given up after a short time.

Engel patented the following process (D. R. P. 15218):—Suspending *magnesia* or natural magnesite in a solution of potassium chloride, and passing in carbon dioxide under pressure, when a double carbonate of potassium and magnesium is precipitated, which can be decomposed into the single salts by heating or dissolving in water:

$$3MgCO_3+2KCl+CO_2+H_2O$$
$$=2MgCO_3,KHCO_3+MgCl_2.$$

The recovery of magnesia from the chloride would have presented difficulties, but there must have been others as well, for the works started at Stassfurt were soon stopped. Delsol (D. R. P. 39903) patented an addition to Engel's process.

The magnesia-potash process has been worked out more successfully in another shape, principally by Precht, and is now carried out on a large scale. This process starts from the fact that trihydrated magnesium carbonate, treated with KCl and CO_2, forms $MgCl_2$ and solid sesquicarbonate, and that the latter can be transformed into solid magnesium carbonate and a solution of potassium carbonate. The first and principal part of the process is represented by the equation:

$$\underset{\text{Solid.}}{3(MgCO_3,3H_2O)}+\underset{\text{Liquid.}}{2KCl}+\underset{\text{Gas.}}{CO_2}$$
$$\rightarrow \underset{\text{Solid.}}{2(MgCO_3,KHCO_3,4H_2O)}+\underset{\text{Liquid.}}{MgCl_2}$$

Lime-kiln gases (30–35 p.c. CO_2) are passed into a solution, saturated at 20°, of strong potassium chloride (95–97 p.c.), made into a paste with tri-hydrated magnesium carbonate with application of a series of vessels and mechanical agitation. The solid double salt formed is separated by suction from the mother-liquor, and is washed with a solution of $MgCO_3$, until it contains no more than 0·1 or 0·2 p.c. Cl. The mother-liquor, containing a large quantity of $MgCO_3$ and KCl, is utilised in various ways. The solid potassium magnesium carbonate is treated principally by the D. R. P. 50786 of the Salzbergwerke Neu-Stassfurt, which consists in heating it under pressure in agitating boilers to 140°, which produces the reaction:

$$\underset{\text{Solid.}}{2(MgCO_3,KHCO_3,4H_2O)}$$
$$=\underset{\text{Solid.}}{2MgCO_3}+\underset{\text{Liquid.}}{K_2CO_3+9H_2O}+\underset{\text{Gas.}}{CO_2}$$

The $MgCO_3$ formed is anhydrous and reacts too slowly to be re-employed in the first stage; it is either sold as such or converted into anhydrous MgO by calcining. Modifications are described in D. R. PP. 55182, 125987, 143408, 143595, 143409, 141408, 141408, 143594, 144742, 155007, 172313.

According to D. R. P. 143409, the potassium magnesium carbonate is decomposed by water at 80°, yielding K_2CO_3 and a crystalline form of $MgCO_3,3H_2O$, which is used over again.

A third process is described in D. R. P. 172313. The potassium-magnesium carbonate, stirred up in water, is decomposed at 40° by magnesia (hydrated or anhydrous), yielding solid $MgCO_3,3H_2O$ and a solution of K_2CO_3.

Sometimes the first process is combined with the second or third, commencing the decomposition by the latter and finishing it by the first. Another modification is described in D. R. P. 135329 of the Deutsche Solvaywerke, 157354, 188504.

In 1885, Borsche and Brünjes patented the production of carbonate from chloride or sulphate by means of ammonium-magnesium carbonate and carbon dioxide.

Wittjen and Cuno (D. R. P. 19197) employ zinc compounds in lieu of magnesium compounds for a similar process.

Scheele's process, treating an alkaline chloride with *litharge*, has been repeatedly attempted without practical success. It has been applied to potash by the Société anonyme Lorraine industrielle (D. R. P. 23701), and by D. C. Knab.

Gilchrist Thomas (D. R. P. 30209) treats alkaline chlorides in the shape of blocks in a heated converter with *pig iron*, containing little carbon, but upwards of 4 p.c. silicon, in a stream of hot air and superheated steam.

Wagner, in 1865, proposed precipitating potash by *hydrofluosilicic acid*, and decomposing the potassium fluosilicate by lime.

Several inventors utilise the slight solubility of potassium *bitartrate* (Goldenberg) and *binoxalate*. Bohlig decomposes the latter by magnesium carbonate. None of these processes is practicable.

The decomposition of alkaline chlorides by the *galvanic current* has been frequently attempted. This process has been applied to carnallite by Wollheim (D. R. P. 16126); at Aschersleben it was to be tried on a large scale with machines of 120 h.-p. The Griesheim Chemical

Company at Frankfort have carried out the electrolytical manufacture of caustic potash and chlorine from strong potassium chloride with great success, and on a very large scale, for some years past, but it is not known by what special process.

(2) *From sulphate.* Leblanc's process will be described below. It has been extended to a direct treatment of *schoenite* by Vorster and Grüneberg, and Precht (in 1885) even patented a direct addition of magnesium sulphate to the potassium sulphate employed for that process. Clemm (1863) and Precht (1858) decompose schoenite by heating with *coal*, whereupon a mixture of magnesia and potassium sulphide is formed, which is treated with moist carbon dioxide.

Of the processes in which compounds of barium, strontium, aluminium, &c., also aluminium phosphate, are employed for decomposing alkaline sulphates, we mention only the process of Jannasch (D. R. P. 51224), in which potassium sulphate, obtained by a special process from kainite, is boiled with finely ground native barium carbonate (witherite). As the native mineral and no carbonic acid are employed, the decomposition is sure to be incomplete.

E. Pfeiffer states (Zeitsch. f. Chem. 8, 1338, 1375) that he decomposed, for some time, potassium sulphate with barium carbonate on a large scale. W. Bramley has patented the same process in a slightly modified form (Eng. Pat. 1050, 1886).

Dupré (D. R P. 47037) mixes solutions, saturated at 0°, of equivalent quantities of potassium sulphate and sodium carbonate (containing 85 grams Na_2CO_3 and 139 grams K_2SO_4 per litre), and cools down very cautiously below 0°, passing a stream of CO_2 into the liquid; or else 140 grams sodium bicarbonate +140 grams potassium sulphate, dissolved in 1 litre water, are cooled down to −6°, when 200 grams of Glauber's salts crystallise out, which are separated from the solution of potassium bicarbonate by a centrifugal machine. At −10° the separation of Glauber's salts is more complete, but then the process is interfered with by the formation of cryohydrates. A further patent (D. R. P. 52163) contains important improvements of the process.

Vogt and Figge (D. R. P. 31675) convert alkaline sulphates into a porous form by mixing them with silica, clay, magnesia, or lime, calcining, and moulding into small pieces. These are introduced into upright iron cylinders, in which the sulphate is first converted into sulphide by the action of carbon monoxide at a bright-red heat, carbon dioxide being given off, and then into carbonate by the action of carbon dioxide and steam at a lower temperature. These cylinders are combined to a set, into which carbon monoxide is passed at one end and hydrogen sulphide passes out at the other end. The cylinders are discharged from the bottom; the mass is lixiviated, and the porous substance employed over again. This process was to be tried on a large scale at the Aschersleben works; it does not seem to have been successful.

Kayser (Amer. Pat. 320256) converts alkaline sulphates into carbonates by a mixture of equal volumes of CO_2 and CO at a low red heat; SO_2 escapes, and is utilised for converting chloride into sulphate.

Römer (D. R. PP. 66533, 67320, 67780) dissolves potassium sulphate (or schoenite) and potassium dichromate in water at 60° or 80° and neutralises exactly with milk of lime, whereby the following reaction is produced:

$$K_2SO_4+K_2Cr_2O_7+Ca(OH)_2 =2KCrO_4+CaSO_4+H_2O.$$

The precipitated gypsum is removed by filtration, the remainder of it by precipitation with potassium carbonate, or by evaporation *in vacuô* at 80°. The solution of potassium chromate is concentrated by evaporation, cooled down and treated with CO_2, whereby potassium dichromate and bicarbonate are produced. The former crystallises out and $KHCO_3$ remains in solution. By boiling this down to 45°-50° Bé., CO_2 escapes and K_2CO_3 is obtained.

At the Buckau Chemical Works (Fischer's Jahresb. 1894, 469), kainite is treated with sulphuric acid, the escaping HCl being condensed. The solution is decomposed by milk of lime, separated from the gypsum formed and treated with barium sulphide. After removing the barium sulphate, the solution of sulphides is decomposed by carbon dioxide (converting the H_2S given off into sulphuric acid); the alkalis are converted into bicarbonates and the sodium bicarbonate crystallises out on cooling, leaving potassium bicarbonate in solution.

Potassium carbonate by the Leblanc process.

This process consists in fusing potassium sulphate with calcium carbonate and coal. Both the theory and the practical execution of this process are exactly like its original application to soda, to which we must refer for particulars. This also holds good for the furnaces, lixiviating apparatus, boiling-down pans, &c. We shall here point out only those matters in which the potash process differs from the soda process.

The potassium sulphate is nearly always that obtained by decomposing potassium chloride with sulphuric acid. That obtained from schoenite is too light, and is easily carried away by the draught. Without damaging the process, some schoenite may be mixed with the K_2SO_4.

The furnaces are almost exactly like black-ash furnaces; the only difference is that the hearth is made a little 'dished'—that is, with a depression of 2 ins. in the centre—to counteract the tendency of the melting mass to penetrate into the hearth and raise it up.

The usual mixture is: 100 potassium sulphate, 80 to 90 limestone, and 40 to 50 coal; but on starting a new furnace the proportion of limestone and coal is somewhat increased until the furnace has attained its full heat. Small batches (of 2½ to 3 cwt. sulphate) are finished in 40 to 50 minutes, large batches (up to 5 cwt. sulphate) in about 75 minutes, so that there is no advantage with the latter; on the contrary, small batches are more easily worked, and the furnace suffers less; there is also less volatilisation of potassium compounds. Usually thirty batches of 3 cwt., or thirty-five of 2½ cwt., of sulphate are turned out in 24 hours.

Towards the end of the operation the fusing mass becomes thinner than with soda; the end of the operation is at hand when the evolution of 'candles' begins to diminish slightly, whereupon the batch must be drawn out at once. The temperature rises from 700° at the beginning to 900°C. at the end.

Good black ash from potash should contain 40 to 45 p.c. potassium carbonate (counting the hydroxide as such), and not above 0·5 to 1·5 undecomposed sulphate, and 0·5 to at most 1·0 sulphide. The less limestone and coal are used in the first stage the less caustic it contains Cyanide is formed from the nitrogen of the coal, sometimes to such an extent that the recovery of ferrocyanide is a paying process. German coal yields less cyanide than English (Newcastle) coal.

100 parts of potassium sulphate, with an average proportion of limestone, yield from 157 to 163 parts of black ash.

The black ash is left to cool for 1 or 2 days, and is broken up in smaller pieces than with soda (say, not above 4 ins. diameter). The lixiviation takes place precisely as with soda. For each ton of black ash to be lixiviated in 24 hours there should be vat space amounting to from 250 to 350 cubic feet. The water is used in summer without heating; in winter about 30°C.; the 'strong vat' should be about 40° to 45°C. The strong liquor, as it is run off, tests from 36° to 60°Tw.; the average is 42°Tw. It is greenish-yellow, sometimes with a reddish cast. It contains all the same impurities as soda tank-liquor. Pfeiffer quotes the following quantities found in two samples, calculated upon 100 parts of K_2CO_3 (+KOH):

	a	*b*	
Potassium sulphate .	3·27	4·34	parts
,, sulphide .	3·17	2·35	,,
,, thiosulphate	1·72	3·61	,,
,, silicate .	1·98	2·24	,,
Total sulphur (as K_2SO_4)	9·6	11·36	,,

There is also aluminate, ferrocyanide, ferrosulphide, &c. The *tank-waste* ought not to contain above 0·2 to 0·3 p.c. of soluble potassium carbonate.

By directly evaporating the tank-liquor to dryness, and calcining, a yellow or reddish potash is obtained which must be purified by redissolving, bringing again to dryness, and calcining. It is decidedly preferable to *carbonate* the tank-liquors exactly as is done with soda liquors, whereby the hydroxide and sulphide are converted into carbonate, and the ferrous sulphide is precipitated. This can be done by gaseous carbon dioxide in the manner described for soda, or very advantageously by means of potassium bicarbonate.

The *evaporation* of the liquor takes place in pans heated by the waste fire of the black-ash furnace either from the top or the bottom. Pans fired from the top suffer less, and the evaporation takes place more quickly than with bottom heat, which requires about twice the heating surface; still, bottom-fired pans are generally preferred in potash works, because the liquors are less contaminated with SO_2, soot, coal-ashes, &c.

The evaporation can be carried on with good liquors to 77°Tw. before any sulphate 'salts out.' At this point the liquor is run off into coolers, where most of the sulphate is precipitated in a muddy form, together with a little $K_2CO_32H_2O$. With inferior liquors, containing much sulphate, the sulphate may 'salt out' even at 60°Tw., and this takes place in any case above 77°Tw. up to 123°Tw., at which point all the sulphate will have been removed. That part which is precipitated in the pans during evaporation would, in bottom-fired pans, produce very inconvenient crusts unless it were constantly removed by 'fishing.' This can be done most conveniently with boat-pans or by Thelen's mechanical fishing-pans. In the case of top-fired pans such deposits are harmless, and hence at some works they employ bottom-heat up to 77°Tw., and top-heat above that point.

The potassium sulphate, precipitated both in the pans and by cooling the liquor, is drained, freed from adhering liquor by cold water, and used over again in the black-ash furnace; this is an advantage over the Leblanc soda process, where the sulphate remains with the soda-ash, and is thus lost. When using coal containing much nitrogen it pays to extract the potassium ferrocyanide, which is found together with the sulphate. The deposit is for this purpose dissolved by water and steam to sp.gr. 66½°Tw.; the solution is clarified and run into coolers, where the ferrocyanide crystallises out. It is purified by re-dissolving to 60°Tw. The yield is generally below 1 p.c. of the carbonate.

The *finishing operation* takes place in a calcining furnace, similar to those employed for soda, but always connected with a cast-iron pot or a wrought-iron pan, set at the end opposite the fireplace, for utilising the waste heat. In those pans the liquor is brought to at least 123°Tw., and sometimes to the state of paste. In the latter case the furnace-bed is made level; when intended for liquor of 123°Tw. it must be made to slope down from the working-door to a depth of 5 or 6 inches. In any case the furnace must be brought to a bright-red heat before charging it with fresh liquor or paste, so that a crust is formed at once on the bottom, and there is less tendency for the liquor to penetrate into the furnace-bed, which, of course, must be made with the greatest care, exactly like that of a black-ash furnace. The new crusts forming at the surface must be worked down, and when the whole mass is dry it must be detached from the brickwork and broken up by means of the 'rake' and the 'paddle.' In the intervals of working the mass the heat is raised by closing the door and stirring the fire until the surface shows just incipient fusion, but not above this point. When the mass has been brought to a red heat throughout, and into the state of a uniform powder, it is drawn out and is left to cool on an iron plate. With liquor of 123°Tw., four or five batches of 5 or 6 cwt. of potash can be turned out in 24 hours. It is important to avoid any interruptions of work, which nearly always produce cracks in the brickwork.

With carbonated liquors a single calcination furnishes a marketable product containing 85 to 92 p.c. carbonate, 10 to 2 sulphate, 2·5 to 0·5 chloride, and a little insoluble matter. This is, however, frequently *refined* by redissolving it with the aid of steam, in tanks provided with a suspended sieve or with a mechanical stirrer, to a strength of 110° or 112°Tw., and allowing it to settle, when, on cooling, most of the sulphate crystallises out. The clear liquor is further concentrated to 123°Tw. in the pans behind the calcining furnaces, and is calcined with special care. This refined product contains:

Potassium carbonate (hydroxide, silicate, aluminate)	from 92 to 98·5 p.c.
Sodium carbonate .	„ 2·5 „ 0·5 „
Potassium chloride .	„ 2·5 „ 0·6 „
Potassium sulphate .	„ 3·0 „ 0·4 „

The quantity of silicate and aluminate is very slight. Phosphate, which always occurs in potash from vegetable sources, is absent here.

Hydrated potassium carbonate. For some purposes, especially for flint-glass making, potash entirely free from sulphate, but containing 12 to 18 p.c. of water, is manufactured as follows. Ordinary carbonate is dissolved to a strength of 142°Tw., or even above this; the solution is allowed to cool and settle, which causes nearly all the sulphate to separate. The clear liquor is evaporated in flat-bottomed pans to the state of a thick paste; the fire is now drawn, and the mass is constantly stirred till it has been converted into a coarse powder. It is less deliquescent than calcined potashes; its composition approaches the formula $K_2CO_3,2H_2O$.

3. *Potash from felspar and other rocks.* The recovery of potash from rocks containing it in large quantities (sometimes up to 14 p.c. K_2O), which undoubtedly by their decomposition have furnished all the potash existing in the soil, and hence indirectly that obtained from vegetable and animal sources, has been attempted by a number of chemists for many years past without much success. The most promising process seemed to be that of Ward and Wynants, in which finely-ground felspar (orthoclase) is ignited with lime and fluorspar until the mass had fritted. On lixiviation potassium hydroxide and silicate are decomposed by means of carbon dioxide. The silica is precipitated, and potassium carbonate can be obtained from the solution in a very pure form. Both this and all similar processes are quite out of the field, since the discovery of the Stassfurt deposits has opened out an incomparably more convenient source of potash, which is, at any rate, sufficient for hundreds of years to come. The proposal of Spiller (J. Soc. Chem. Ind. 1882, 128), to heat felspar with calcium fluoride and sulphuric acid in order to obtain potassium and aluminium sulphate, has very little prospect of practical realisation.

E. Hart (U.S. Pat. 997671) prepares potassium sulphate from potassium-bearing rocks by fusing them with barium sulphide so as to give a glass, and extracting the potassium from the powdered product by a mineral acid. Potassium alum, for instance, is obtained by fusing 1 mol. orthoclase with 1 mol. barium sulphate and 2 at. coal and treating the product with sulphuric acid.

Thompson (U.S. Pat. 995105) mixes finely ground felspar with an alkaline acid sulphate and chlorides, say, 5 felspar, 5 acid sodium sulphate and 1·8 sodium chloride, keeps the mixture at a red heat for 2 or 3 hours, grinds it after cooling, lixiviates and allows the solution to crystallise. The acid sulphate, acting on the chlorides, liberates hydrogen chloride, which at the high temperatures acts upon the felspar with formation of potassium chloride; this, with the $NaHSO_4$, forms again HCl and K_2SO_4. In this way, he asserts, 80 to 90 p.c. of the potassium contained in felspar is recovered as sulphate.

Herstein (J. Ind. Eng. Chem. 1911, 426) fuses felspar with calcium chloride and a like quantity of calcium carbonate in revolving furnaces; potassium chloride escapes in the state of vapour, while cement clinker remains behind.

4. *Potash from wood-ashes.* This was formerly the only source of potassium carbonate on a large scale. About the middle of the last century it lost much of its importance through the rise of the vinasse industry; and, since the manufacture of potassium carbonate by Leblanc's process has more and more extended, that made from wood-ashes has correspondingly receded into the background. Nor is this result very much to be deplored, for the ready sale formerly obtained for potash from wood-ashes led to the devastation of forests at an alarming rate. On the other hand, it is a fact that in some localities the only use to be made of timber is its conversion into ashes, and extraction of potash therefrom; but the places where this can be called in any way a rational process are getting more and more scarce. Several of the brands formerly found in trade have become extinct. Since the use of wood as fuel has also very much diminished during the last generation the collecting of ashes from this source, which were formerly sold to the potash manufacturers, is now too troublesome in most countries, and such wood-ashes are there only used for domestic and agricultural purposes. Only some parts of Russia, Transylvania, Illyria, Canada, and the United States, still continue to furnish supplies of commercial pot-ashes (pearl-ash, &c.).

Potash is an indispensable element for the growth of most plants, and hence is found in their ashes. But where it is associated with much silica and phosphoric acid the ashes contain but little carbonate, and are not available for the manufacture of potash. This, for instance, holds good of straw-ash. The only practically important source of potash is *wood-ash*; it is true that the ashes of several herbaceous plants contain a great deal more of potassium carbonate than the ordinary woods, and it has been actually proposed to grow such herbs for this manufacture; but this is irrational and without any hope of success, as these quickly growing plants exhaust the soil much more quickly than can be made up by the natural decomposition of the minerals composing it.

The following table shows the percentage of total ash and of potash in some of the more important woods and plants:—

	Ash per cent.	Potash per cent.
Pine wood	0·34	0·045
Poplar wood	—	0·075
Beech wood	0·58	0·145
Beech bark	—	0·153
Ash wood	1·22	0·074
Oak wood	1·35	0·153
Oak bark	—	0·420
Box wood	—	0·226
Willow wood	2·80	0·285
Elm wood	2·55	0·390
Vines	3·40	0·550
Thistles	—	0·500
Rush	—	0·508

	Ash. per cent.	Potash per cent.
Ferns	3·64	0·626
Nettles	—	2·503
Vetch	—	2·750
Wormwood	—	7·300

In Canada most potash is made from elm, birch, larch, and maple.

The potash is contained in these plants in the shape of sulphate, chloride, silicate, and organic salts. The latter, on calcining, are converted into carbonate, part of which may be converted into hydroxide on lixiviation if lime is present; any silica present will pass into potassium silicate, and this renders the manufacture of potash from straw quite irrational. Where soda is present in large quantities the potash obtained must also be of inferior value. Hence the quality of potash found in trade is very varying, quite apart from actual falsifications with coal-ashes, soda, &c.

The manufacture of commercial potash is a very crude process. The wood is burned in pits dug in the earth in places sheltered from wind. The collected ash (beech-wood ash is preferred to all other wood-ashes; vine stalks, ferns, &c., where obtainable in quantity, are still better) is spread on a stone floor, sprinkled with water, and worked through until it is evenly damp. Sometimes (in Canada) a little lime is mixed with it, which afterwards causes the formation of caustic potash. The damp ash is placed in casks provided with a false bottom, covered with straw, and water (preferably hot) is poured over it. After some time the liquor thus formed is drawn off by a plug-hole at the bottom; if it is about 32°Tw. strong it can be boiled down at once; the weaker liquors and washings are used for lixiviating fresh ash. The residue, which with this rough style of working still contains much potash, is a good manure.

The boiling-down is also generally a very rough process. In lieu of pans possessing a large heating-surface (pans fired from the top would be the best) usually circular cast-iron pots fired from below are employed, in which the liquor is boiled down to dryness. In spite of stirring up the mass before it becomes quite dry much of it burns fast to the pot, causing a great waste of fuel and a speedy destruction of the pot. In America the mass is heated nearly to redness, and is converted into greyish-pink compact 'pot-ashes,' which are assorted by official inspectors into 'firsts,' 'seconds,' 'thirds,' and 'unbrandables.' The brown crude pot-ashes are calcined in reverberatory furnaces, which causes the carbonaceous and other organic matter to burn away, the hydroxide to be carbonated and the sulphide, &c., to be converted into sulphate. An excess of heat has to be avoided, because the mass would then fuse, and this would prevent the organic substance from being burned. The resulting product should be white or blueish—the latter from potassium manganate. A purer product is obtained by dissolving the product of calcination in water, separating the liquor from the insoluble substances, evaporating and calcining again; the American 'pearl-ashes' are thus made.

The common American 'pot-ashes' are frequently made with addition of so much lime that they contain the major portion of the potash in the caustic state; thus some of the silicate is also recovered which would be lost otherwise. This potash fuses below a red heat; it is therefore only boiled down until the mass solidifies on cooling and appears in grey, red, or black lumps. This description of potash must be even more carefully protected against atmospheric moisture than ordinary commercial potassium carbonate, although this is also deliquescent. Such caustic potash is very much in request by soap makers; it takes less lime in making their lye, and causes less loss, just in proportion to the smaller amount of lime-mud.

'Purified carbonate of potash' is made from ordinary carbonate in two different ways. In one the carbonate is stirred up in an iron pot with 1½ or 2 times its weight of *cold* water, and the mixture which gets hot allowed to cool down before siphoning off the clear liquor. The sulphate and some chloride remain behind, together with the insoluble matter; the residue is not washed (which would cause the sulphate to be re-dissolved), but only pressed. The liquor, containing mostly carbonate, but also chloride and silicate, is brought to dryness, stirring it up to the end. In the other the solution is made with *hot* water, the residue is exhausted in the same way, the liquors are boiled down to sp.gr. 1·50 and allowed to cool, when the sulphate and some chloride crystallise out. This process is more expensive than the former. In order to make still purer carbonate for flint-glass manufacture, pearl-ashes are calcined with a little sawdust, lixiviated, the clear liquor is boiled down and calcined, and this is repeated twice over; the last product is dried down until it is converted into granular 'crystallised' carbonate with 15 to 18 p.c. of water.

According to Chem. Zeit. Rep., 1908, 3, potashes are manufactured from the stems of sunflowers in 24 factories in Northern Caucasia, to the extent of 100,000 to 120,000 tons per annum.

The potash from bamboo-cane, made in British Burmah (Romanis, Chem. News, 45, 158), testing 32·54 K_2O, 0·98 Na_2O, 18·72 KCl, 16·95 SiO_2, 8·07 CO_2, 2·71 SO_3, 1·10 Al_2O_3 and Fe_2O_3, 19·43 H_2O, partakes more of the nature of a silicate than that of a carbonate (like all other potashes made from graminaceous plants).

The quantity of wood potash produced in the whole world was estimated by H. Grüneberg, in 1873, at 20,000 tons per annum. Even then its production had very much receded in comparison with former times. The exportation from Russia, formerly the leading country in that respect, which in 1864 had been 11,000 tons, in 1873 had declined to 5540 tons; New York, which in 1865 exported 2610 tons, in 1873 only exported 388 tons. Of the American exportation, about one-tenth is pearl-ashes, nine-tenths caustic pot-ashes. At present the total quantity of wood potash annually produced cannot exceed 10,000, or at most 15,000 tons; a great part of this is consumed in the countries where it is produced.

5. *Potash from beet-root vinasse.* In the last stage of the manufacture of sugar from beet-root a syrupy liquid is obtained, which, although containing a very large quantity of sugar, cannot be brought to crystallisation, owing partly to the presence of organic impurities, but chiefly to

Analyses of Commercial Potashes, Pearl-ashes, &c., from Wood.

Origin	Quality	K_2CO_3	KOH	Total available alkali calc. as K_2CO_3	Available potash calc. as K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Analyst
American potash .	—	68	—	75·5	68	5·8	15·3	8·1	Pesier
,, ,,	1	41·7	49·6	108·2	106·4	1·4	4·0	2·0	F. Mayer
	2	19·4	44·4	87·8	77·2	8·2	16·1	5·6	
,, ,,	2	18·3	36·6	81·7	65·9	12·2	15·1	14·6	Grüneberg
	2	34·5	29·6	81·8	77·9	3·0	15·0	7·5	
Montreal potash	firsts	43·87–	50·03–	92·49–	88·83–	6·24–	16·07–	4·41–	Tatlock
		26·16	36·50	89·82	85·54	2·84	10·40	1·68	
	seconds	38·53–	42·44–	85·79–	76·24–	11·47–	18·92–	12·82–	
		21·71	30·63	85·08	73·98	8·52	9·18	6·13	
	thirds	46·31	6·14	72·10	53·86	17·81	20·53	7·63	
Canadian pearl-ashes	—	71·3	—	74·2	71·3	2·3	14·3	3·6	Pesier
,, ,,	—	65·0	—	70·2	65·0	4·0	21·0	7·0	Grüneberg
,, ,,	1	77·50	—	80·98	77·50	2·86	11·65	2·65	Tatlock
	—	71·38	—	74·53	71·38	2·31	14·38	3·64	
Tuscan potashes .	—	74·1	—	78·0	74·1	3·0	13·4	0·9	Pesler
,, ,, .	—	62·6	—	76·9	62·6	11·0	15·5	4·5	Grüneberg
Illyrian potashes .	1	89·3	—	89·3	89·3	0·0	1·2	9·5	
Hungarian ,, .	3	44·6	—	68·0	44·6	18·1	30·0	7·3	
Galician ,, .	—	46·9	—	51·6	46·9	3·6	29·9	11·1	
Russian ,, .	—	69·61	—	73·77	69·61	3·09	14·11	2·09	Pesier
,, ,, .	—	50·84	—	66·78	50·84	12·14	17·44	5·80	Bastelaer

the large quantity of salts present. The latter circumstance prevents the utilisation of such 'beet-root molasses' in a similar way to cane-sugar molasses. For a long time the only way of dealing with beet-root molasses was this: diluting them with water, neutralising their alkaline reaction with sulphuric acid, causing the liquor to enter into alcoholic fermentation by means of yeast, and distilling off the spirit (which is of rather inferior quality). The liquor remaining behind in the stills, called 'vinasse' in French or 'schlempe' in German, was formerly always led back upon the fields on which the sugar-beet had been grown. To some extent this is still done; nor can it be denied that this is, after all, the simplest and at the same time the most rational way of dealing with it, wherever carriage is practicable, for in this way the mineral substances (especially potash and phosphoric acid) taken from the soil in the shape of beet-root crops, are given back to it in a soluble form, together with the nitrates formed in the plants, which are lost in every other process of utilising the vinasse.

On the other hand, the large quantity of potash contained in this liquor has, under ordinary circumstances, a greater commercial value, even deducting the expense of recovering it in the shape of potassium carbonate, than in that of liquid manure. This was pointed out about 1830 by Dubrunfaut, to whom is due the introduction of the very important industry of beet-root potash, which, however, did not take firm root until about 1850, first in the north of France, and then in Belgium and Germany. In France this still forms the most usual way of dealing with molasses, whilst in Germany it has become more usual to extract the sugar by means of the osmose, the strontia, and the lime processes. The strontia process easily admits of recovering the potash in the shape of 'vinasse cinder'; but the dilute liquids, obtained by the osmose and the lime process, are usually only applied for manuring the fields. Pfeiffer (Kali Industrie, 101) estimates the potash contained in the beet-root-juice worked in Germany in 1883, calculated as 80 p.c. potassium chloride, at 15,000 tons, 8000 tons of which was rendered back to the fields by the factories working the osmose and substitution processes, whilst 7000 tons passed into molasses. Of the latter, about 1350 tons were recovered in the shape of 'schlempekohle' from the strontia process, and 3000 or 4000 tons from the factories working the molasses for spirit. In France sometimes the osmose liquor is worked for potassium nitrate, which forms 50 p.c. of the 'salin' obtained by boiling down the liquor to 40° Bé. (Dingl. poly. J. 245, 192; 264, 510).

Sugar-beet may be said to yield about 1 p.c. of ash, nearly half of which consists of potash (calculated as K_2O), present in the juice to a great extent in the shape of nitrate and of salts of organic acids, all of which on calcining yield carbonate. Very little of it goes away with the sugar: nearly all remains in the molasses, which contain from 44 to 50 p.c. of sugar, 14 to 18 p.c. other organic substances, 16 to 18 p.c. salts, and 15 to 18 p.c. water; the ash amounts to 10 to 12 p.c. The ash is composed as follows, according to Krocker:

	Soluble	Insoluble
Potash	47·88	1·70
Soda	2·34	0·17
Lime	—	5·08
Sodium chloride . .	12·92	—
Sulphur dioxide . .	1·53	—
Carbon dioxide . .	22·39	4·00
Silica	0·85	0·22
Phosphorus pentoxide .	—	0·29
Lime, magnesia, ferric oxide (as phosphates)	—	0·63
	87·91	12·09

Heidenpriem found in molasses ash:

Potash	47·67	51·72 p.c.
Soda	8·00	11·43 ,,
Lime	3·12	5·04 ,,
Magnesia	0·10	0·18 ,,
Carbon dioxide . .	27·94	28·90 ,,
SO_3,P_2O_5,SiO_2,Cl,Fe_2O_3	6·16	9·33 ,,

Manufacture of vinasse-cinder (*salin, schlempekohle*). The vinasse, a liquid of about sp.gr. 1·028, and always of acid reaction (purposely brought about for the sake of fermentation, *v. supra*), is neutralised with lime, and is then concentrated by evaporation. Since the profitable working of this process depends entirely upon the economical evaporation of a dilute liquid, much ingenuity has been expended on the evaporating apparatus. The heat must act both as top and bottom heat, the flame travelling between two pans, or over the top of a pan covered with an arch, upon which another pan is set so as to be indirectly heated. The most successful and most widely-employed system for this purpose is Porion's furnace, in which the evaporating-surface is largely increased by splashing about the liquid in the fire gases by means of paddle-wheels revolving from 400 to 800 times per minute.

The heat required for evaporating the liquid is produced partly by an ordinary fire, partly by the combustion of the organic substance contained in the vinasse. When the latter has been brought to the syrupy state, say 60°Bé., it is transferred from the iron pan on to the bed of a reverberatory furnace, immediately attached to it, on which it is altogether dried, whereupon it takes fire and itself produces a large amount of heat. This is aided by the nitrates contained in the mass. The heat must, however, be so regulated that the mass is not brought to fusion; when fused it would be difficult to lixiviate, and it would also contain lower oxidation-products of sulphur. The process is therefore finished when a carbonaceous mass has been formed, a sample of which yields with water on filtration a colourless solution. This is the 'salin brut' or 'schlempekohle' (vinasse cinder), a product which was formerly largely sold in this state, and employed chiefly for soft-soap and for the manufacture of saltpetre from Chilean sodium nitrate; it is now generally worked up into potassium carbonate and other salts.

The composition of vinasse cinder varies between very wide limits, according to the soil on which the beet had been grown. Grüneberg (Amtlicher Bericht über die Wiener Ausstellung, 1, 399) gives the following figures as the average composition of this product:

Potassium carbonate . .	30 to 35 p.c.
Sodium carbonate . .	18 to 20 „
Potassium chloride . .	18 to 22 „
Potassium sulphate . .	6 to 8 „
Insoluble (incl. carbon) .	28 to 15 „

but the analyses published by Sauerwein, Gohren, Kuhlmann, Esselens, Lefevre, and others, prove that the proportion of the ingredients may vary even more.

A large number of analyses of vinasse cinder are given by Hinz (Fischer's Jahresb. 1893, 389 *et seq.*).

In lieu of burning the syrupy vinasse on the hearth of an open surface, C. Vincent (Compt. rend. 84, 214) runs it, at a strength of 40°Bé., into iron retorts, and carbonises it with condensation of the formed vapours, the recovered liquids being subjected to a special treatment. This extremely ingenious process, by which trimethylamine and methyl chloride were for the first time obtained as commercial products, together with methyl alcohol and ammonia, was carried out on a large scale at Courrières, in the north of France, but has not extended beyond this. A modification of Vincent's process is that proposed by A. Zwillinger (D. R. P. 38419), who carbonises vinasse, brought to the syrupy state, in a retort by means of superheated steam.

The following description is an outline of Vincent's process. The cinder, obtained by heating the vinasse-residue in closed retorts, is very porous and easy to lixiviate; the potash made from it is very pure, and especially free from sulphate and sulphide. The gaseous products are submitted to a process of condensation quite similar to that usual at gasworks; a little tar and a considerable quantity of aqueous fluid is condensed, and a considerable quantity of gas is left over, which may be used for heating purposes.

The aqueous liquid contains ammonium carbonate, hydrosulphide and cyanide, methyl sulphide, methyl alcohol, trimethylamine, and the volatile monobasic fatty acids. It is neutralised with hydrochloric acid, and the greater proportion of water is removed by distillation. The distillate contains, together with much water, methyl alcohol and methyl cyanide; by re-distilling it with lime, the methyl alcohol can be set free, and calcium acetate remains behind. From 100 kilos. of molasses 1¼ litres of methyl alcohol is obtained. The original liquid, concentrated by distillation and allowed to cool, yields a crop of ammonium chloride (about 2 kilos. for 100 kilos. of molasses). The mother-liquor (about 1·8 kilos.) contains principally trimethylamine hydrochloride. It is further concentrated by evaporation, and the dry mass is subjected to prolonged heating. At 260° there begins a strong evolution of gases, and at 325° the decomposition is finished. The gases escaping consist of trimethylamine and methyl chloride, afterwards with much ammonia; they are passed through hydrochloric acid, which retains trimethylamine and ammonia, whilst methyl chloride passes on, is washed with water and collected in a gas-holder. The liquor is concentrated to a boiling-point of 140°C.; on cooling, nearly all the ammonium chloride crystallises out and trimethylamine hydrochloride remains in the mother-liquor. The gaseous methyl chloride is dried, and by means of compression and cooling is condensed to a liquid, boiling at −23°C., which is sent out in strong wrought-iron or copper drums, and used principally in the manufacture of aniline dyes.

The theory of the decomposition of the dry trimethylamine hydrochloride by heat is as follows. At first this salt is, like ammonium chloride, dissociated by heat, and much free trimethylamine is volatilised. The acid residue at a higher temperature undergoes the following reaction: $N(CH_3)_3,3HCl = 3CH_3Cl + NH_3$. This explains the final decomposition into trimethylamine, methyl chloride, and ammonia.

Elsewhere the recovery of methyl chloride and trimethylamine does not appear to have been attempted, but in several places the ammonia has been recovered by various methods. Thus Baswitz (Dingl. poly. J. 245, 415) runs the vinasse, concentrated to 31° or 41°Bé., in a thin jet into red-hot retorts. The gaseous products pass through a pipe filled with pieces of firebrick and heated outside by waste heat; further on some tar is condensed, rich in pyrrole and pyridine bases, then the ammonia is absorbed in sulphuric acid; finally the methyl alcohol is condensed by cooling, and the uncondensed gases are returned to the fire. Each retort takes a charge of 360 litres of concentrated vinasse every 12 hours; the produce of 4 retorts is: 87·5 kilos. ammonium sulphate, 30 kilos. liquor containing amines, 4 to 4·5 kilos. methyl alcohol, 57·5 kilos. tar. (The process did not pay when the prices of the above products went down.) H. Hirzel (Zeitsch. Chem. 11, 346) employs a vacuum apparatus with mechanical stirrer. Borsche and Sohn (Dingl. poly. J. 244, 85) carbonise the vinasse with lime in order to increase the yield of ammonia; they assert that up to 80 p.c. of the nitrogen can be thus obtained as NH_3. Similar processes are patented by E. Ernst (*ibid.* 244, 86; 245, 413), by Oppermann, by Gaillett, and by the Waghäusel Sugar Company (*ibid.*). Lederer and Gintl (*ibid.*) carbonise vinasse, or the liquors of the lime and osmose process in revolving drums by a continuous process, the gases being treated for the recovery of ammonia.

Other apparatus for treating vinasse are those of Kux (Dingl. poly. J. 247, 163), of Klauning (*ibid.* 261, 256), of Gontard (*ibid.* 258, 498), and of Theisen (*ibid.* 257, 405).

Working-up of the vinasse cinder. The cinder is broken up into pieces of the size of a man's fist, or rather less, and is methodically lixiviated with hot water in the usual way. The liquor is run off at a strength of 23–32°Tw. The black residue (grey after drying) contains from 8–12 p.c. of alkaline salts (partly being potassium sulphate, partly not soluble in water), 20–40 p.c. carbonaceous matter, containing a little nitrogen, 15–30 p.c. calcium carbonate, and a few p.c. of other earthy matters. The first evaporation takes place by means of steam coils, and is carried to 74–82°Tw., the concentration being higher in summer than in winter. Most of the potassium sulphate is now precipitated as a fine mud; after two hours' settling the clear liquor is allowed to cool down, when impure potassium chloride crystallises out. According to whether the salts are at once subjected to methodical washing or not, they contain less or more potassium carbonate, as shown by the analyses of Tissandier (Wagner Jahr, 1868, 286). The analysis of a large number of French samples of such chloride (by Blattner, unpublished) yielded—

Potassium chloride	66·21 to 87·55 p.c.
Potassium sulphate	5·27 „ 19·86 „
Potassium carbonate	0·10 „ 6·49 „
Sodium carbonate	0·40 „ 4·57 „
Water	1·40 „ 8·79 „

This product is principally employed for conversion into sulphate, and then into carbonate, by the Leblanc process.

The mother-liquor is further evaporated by open fire in wrought-iron pans with flat or saddle-shaped bottoms, in three stages, down to 127°–142°Tw. During evaporation, monohydrated sodium carbonate is separated, which must be fished out, and is purified by washing and calcining; on cooling down, to 97°Tw., principally potassium chloride crystallises out. This is washed like that obtained previously, but beyond that strength the crystals consist principally of a potassium-sodium carbonate $K_2CO_3,Na_2CO_3,12H_2O$, together with some hydrated potassium carbonate, $K_2CO_3,2H_2O$. The double carbonate is re-dissolved in a little hot water and evaporated down to 127°Tw., during which operation nearly all the sodium carbonate separates as monohydrated salt, and is removed by fishing. The mother-liquor from this operation is boiled down, together with the mother-liquor formerly obtained, and is, after proper settling, calcined in a reverberatory furnace. It yields a crude potassium carbonate containing:

K_2CO_3	80–84 p.c.
Na_2CO_3	8–10 „
KCl	3–4 „
K_2SO_4	3–4 „
K_2SiO_3	0·25–0·5 „
K_2HPO_4	0·3–1·5 „
Insoluble	0·1–0·2 „

Bauer (D. R. P. 191105) obtains technically pure potassium carbonate from vinasse cinders by heating the solution to 53°Bé., separating the precipitated salts, heating the purified solution to 90°, until a concentration of 56°-62°Bé. is attained and allowing to cool, whereupon potassium sodium carbonate crystallises out and is decomposed into K_2CO_3 and Na_2CO_3 by fusing and keeping at 50°.

Part of the potassium sulphate is formed from thiocyanate; and this salt itself is partly formed during the evaporation from potassium ferrocyanide and sulphide as witnessed by the ferrous sulphide, always precipitated together with the fished out soda. This purification from iron is very important, and is sometimes promoted by purposely adding potassium sulphide to the liquors in sufficient quantity to precipitate the iron. Otherwise, even white potash is discoloured on contact with the air. Once calcined potash, when treated as above, is sufficiently pure and white, but otherwise it can be purified by re-dissolving, settling, and recalcining. The analyses given at top of next page show the position of different descriptions of vinasse potashes.

6. *Potash from suint.* The 'suint' or 'yolk,' which forms a third or more of the weight of raw sheeps' wool, was proved by Chevreul to contain, together with many other substances, a considerable quantity of potash, combined with fatty acids to form a soluble soap. Maumené and Rogelet were the first, in 1859, to utilise this for recovering potassium carbonate from the wool used at and near Rheims and Roubaix, and their example has been followed elsewhere, but not to any great extent. 100 parts of raw wool are stated by Maumené to yield from 14 to 18 parts of salts, or about 5 parts of potassium carbonate; hence the 60,000 tons of wool annually imported into the United Kingdom ought alone to yield about 3000 tons of potassium carbonate, none of which is recovered up to the present. Even at Roubaix, Rheims, and Elbeuf, in lieu of the 1200 tons obtainable from the wool consumed there, only 150 tons per annum are actually recovered; the total production of suint potashes in France, Belgium, and Germany probably does not exceed 2000 tons per annum. This is all the more to be regretted as the potash contained in suint in the ordinary course of washing raw wool in a

ANALYSES OF COMMERCIAL VINASSE POTASHES.

Origin	K_2CO_3	Na_2CO_3	K_2SO_4	KCl	Insol.	H_2O	Analyst
French potash . . .	53·9	23·1	2·9	19·6	—	—	Pesier
Valenciennes potash . .	79·0	14·3	3·9	2·8	—	—	Grüneberg
Refined potash . . .	92·68	3·98	0·43	2·45	0·06	0·50	Tatlock
,, ,, . . .	91·22	2·89	2·76	1·92	0·08	0·85	,,
,, ,, . . .	90·83	2·68	2·67	2·52	0·27	0·90	,,
,, ,, . . .	90·25	2·52	3·81	2·92	0·21	0·45	,,
Belgium crude ash . .	43·0	17·0	4·7	18·0	—	—	Grüneberg
,, ,, . .	34·3	13·0	11·0	23·5	—	—	,,
Magdeburg crude ash .	32·9	18·5	14·0	16·0	—	—	,,
,, ,, .	27·1	18·0	10·0	9·5	—	—	,,
Wäghäusel (refined) . .	94·39	trace	0·28	2·41	0·18	—	v. Groningen
,, ,, . .	88·73	6·45	2·27	1·01	—	—	Keller
,, ,, . .	78·10	13·33	2·31	3·21	3·05	—	Tissandier
,, ,, . .	81·22	13·15	1·78	3·25	0·80	—	,,
,, ,, . .	91·25	4·73	0·80	2·61	0·61	—	,,

running stream does not return to the soil, but merely contributes to the pollution of water-courses. But the difficulty in the way of the general adoption of the recovery process is, that it does not pay on the small scale, and that neither producers nor consumers of wool, in the majority of cases, will relegate the scouring of their wool to a central manufactory, where it is doubtful whether the different parcels can be kept entirely distinct. It is thus preferred by most wool-growers to wash their own wool, and, if possible, to bring the washings again upon their meadows.

The process for working the wool for suint potash is as follows. Instead of washing the raw wool first in a running stream, and afterwards scouring it with soap, soda, or putrefied urine, the wool is, before the proper scouring process, submitted to a methodical lixiviation with cold water, either in a series of casks or tanks, or in mechanically-acting washers, for instance that constructed by H. Fischer (Dingl. poly. J. 218, 484; 229, 446). The dilute washings are always utilised for the first treatment of a fresh quantity of wool. Thus a brown liquor of about sp.gr. 1·12 is obtained, which is evaporated in iron pans of very different constructions where the fuel can be efficiently utilised—for instance, in the reverberatory furnace of Werotte, in which the flame is drawn through the liquid itself by means of an exhauster; or by means of discs fixed on a shaft revolving in the boiling-down pan. Thus a pasty mass is obtained, which is either calcined in an open furnace or submitted to destructive distillation in gas retorts, in order to recover ammonia and illuminating gas. The carbonaceous residue is lixiviated and the liquor is treated similarly to that obtained from vinasse cinder, producing, by fractional evaporation and crystallisation, successive crops of potassium sulphate and chloride. But as suint contains but little soda (in the case of inland-fed sheep only 2·3 Na_2O to 100 K_2O, with sheep fed on the sea coast 13 Na_2O to 100 K_2O), the crystallisation of the double carbonate of potassium and sodium does not take place, the liquor being directly brought to dryness and calcined.

Suint potash, if unadulterated, in fact contains but little soda, as can be seen from the following analyses:—

	From Verviers					First quality		Second quality
	Tissandier			Werotte		Tatlock		
K_2CO_3	71·52	79·01	72·25	68·50	64·30	91·20	89·41	80·57
Na_2CO_3.	4·96	5·15	5·14	3·20	3·10	4·39	3·83	2·48
K_2SO_4	2·48	3·03	3·33	2·10	2·49	0·52	0·17	4·75
KCl	5·88	6·12	7·04	12·50	16·88	1·97	1·67	4·51
K_2SiO_3	—	—	—	8·50	8·00	—	—	—
Insoluble	11·98	5·28	11·19	1·48	1·55	0·04	0·06	0·30
Water	2·83	1·20	1·05	2·77	2·80	1·60	4·70	7·25

The following analyses, by W. Graff, give the composition of wool potash, made in Germany—viz. (*a*) by the simple steeping process, (*b*) and (*c*) by methodical lixiviation:—

	a	*b*	*c*
K_2CO_3 . . .	31·16	75·01	71·40
K_2SiO_3 . . .	17·44	0·62	1·50
K_2HPO_4 . . .	0·50	0·71	
K_2SO_4 . . .	2·00	4·12	5·32
KCl . . .	3·93	5·68	6·74
Na_2CO_3 . . .	3·15	3·07	4·55
H_2O . . .	1·22	1·30	4·72
Insoluble . . .	40·60	9·49	5·77

Potassium hydroxide (*Caustic potash*). The majority of soap-makers prefer causticising their own potassium carbonate, as they mostly do not require to do this thoroughly. Still the manufacture of caustic potash in the solid state is carried on to some extent on the large scale, with black-ash made by the Leblanc process from potassium sulphate, precisely in the same manner as caustic soda is made, so that we can refer to that article. In this place we need only give the analyses (by Tatlock) of some samples of caustic potash made on the large scale :—

——	White	Brown or cream	
Potassium hydroxide	77·64	75·64	74·05
Potassium carbonate	4·62	2·54	3·14
Potassium sulphate	0·38	0·21	0·69
Potassium chloride	2·29	0·93	2·26
Potassium nitrite	0·87	—	—
Sodium hydroxide	4·67	2·59	3·20
Soluble silica and alumina	0·30	0·20	0·55
Insoluble matter	0·02	0·22	0·69
Water	8·84	17·80	15·80
Available potash, K_2O	68·33	65·24	64·31
Available alkali, calculated as K_2O	73·83	68·28	68·08

Graff (D. R. P. 88003) prepares potassium hydroxide from vinasse cinder. The solution of this product is causticised, concentrated by evaporation, separated from the potassium sulphate and chloride crystallising out and now contains only sodium and potassium hydroxides. The necessary quantity of potassium carbonate is added to convert the sodium present into the double salt $KNaCO_3$, which is removed by concentration and cooling, leaving pure KOH in solution. Or else the potassium hydroxide is separated from the potassium-sodium carbonate by evaporating the mixture to dryness and extracting the KOH by means of alcohol.

N. T. Bacon (D. R. P. 99344) employs a hot, concentrated solution of strontia into which solid potassium carbonate is introduced. The conversion into KOH and $SrCO_3$ is almost instantaneous.

The Chemische Fabrik Griesheim (D. R. P. 108500) gives detailed prescriptions for the purification of caustic potash solution by diffusion. The Salzbergwerk Neustassfurt (D. R. P. 117748) effect such a purification by fractionated crystallisation at 60°.

I. A. Reich (D. R. P. 161795) prepares caustic potash by boiling potassium silicofluoride with caustic lime.

Crystallised potassium hydroxide is obtained by Salzbergwerk Neustassfurt (D. R. P. 189835) by conducting the concentration of the solution in a special manner.

Potassium silicate. Potassium silicate, or soluble potash glass, has approximately the formula $K_2O,4SiO_2$. It is prepared exactly like the more common soluble soda glass, by fluxing together white sand and potassium carbonate in a reverberatory furnace, preferably with a little charcoal, which aids in expelling the carbon dioxide by reducing it to monoxide. The following proportions are stated by N. Fuchs to be suitable: white quartz sand 45 parts, commercial potashes 30 parts, wood charcoal 3 parts, to be fused for 5 or 6 hours until no more gas escapes; the product is 58 parts of silicate. O. Schür prescribes: 90 sand, 62·5 potashes, 1·5 charcoal; product 112·5 to 115 soluble glass. Some manufacturers employ potassium sulphate in lieu of carbonate, together with a larger proportion of charcoal, but this process is much more difficult than with carbonate. Solid potassium silicate is a transparent glass, tinged a bluish green, which is either sold as such, or in the state of a thick solution, produced by boiling it with water for a long time, preferably under pressure. Frequently a mixed silicate of soda and potash is produced, either by using a mixture of potash and soda in the fluxing process, or by mixing the solutions.

Potassium silicate can be obtained also by dissolving very finely-divided silica (in the shape of ignited and ground flints, or of kieselguhr, or Farnham stone) in a very strong solution of caustic potash, by prolonged boiling, or in a shorter time by boiling under pressure. This process is actually used for the manufacture of sodium silicate.

The following analyses, by Tatlock, show the composition of commercial potassium silicate :—

——	Solid			Liquid	
	a	*b*	*c*	*d*	*e*
Potash (as silicate)	23·54	22·91	9·46	4·31	3·49
Soda (ditto)	1·28	1·28	1·52	4·20	1·80
Silica	65·60	66·84	23·28	24·32	16·64
Potassium sulphate	0·87	1·08	0·67	0·61	1·48
Potassium chloride	0·48	0·48	0·41	0·67	3·52
Alumina and ferric oxide	0·40	0·32	—	—	—
Water	7·83	7·09	64·66	65·89	73·07

The total quantity of potassium silicate manufactured is but small in comparison with that of sodium silicate; for mixing with soap it can be nearly always replaced by the cheaper sodium silicate. It is, however, used in fresco painting, and for a few other purposes.

Potassium nitrate (*Saltpetre*, *nitre*). Potassium nitrate KNO_3 is first mentioned by Geber, in the eighth century, and again by the alchemists of the thirteenth century. Agricola in 1546 gives a description of its manufacture from saltpetre earth, which does not materially differ from the present process. The artificial preparation of this substance from Chilean sodium nitrate is comparatively a recent process, due in the first instance to the greatly-increased demand produced by the Crimean war, but this manufacture has gained very large dimensions, and is now much more important than the working of natural saltpetre earths.

I. *Manufacture of saltpetre from natural saltpetre earths.* Such earths are found principally in East India, where the district of Tirhût, in Bengal, is the most important one in this respect, and whence nearly all the natural saltpetre still manufactured is derived. Smaller deposits are found in Egypt, Persia, Hungary, Apulia, Kentucky, &c., none of which is of more than local importance now.

The raw material occurs only occasionally in real strata or nests; it is mostly a product, continually re-formed by the action of atmospheric air upon nitrogenous organic matter in the presence of bases, such as lime, magnesia, and potash (for which, in Peru, near the sea-coast, soda is substituted). The organic nitrogen is not simply oxidised by atmospheric oxygen; the process of 'nitrification' never takes place except in the presence of certain microbes, as first proved by Schlösing and Müntz (Compt. rend. 84, 602; 85, 1018; 86, 892), and confirmed by many subsequent observers.

Whether the formation of ammonia is an indispensable intermediate link remains an open question. The nitrification process is, of course, much more intense in hot countries, where it is promoted by the abundance of organic matter, and by the moist and warm atmosphere. It is always dependent upon a supply of nitrogenous organic substances, and has nothing to do with the direct formation of nitric acid from atmospheric oxygen and nitrogen by the electric discharge. Saltpetre earth is, consequently, chiefly found in the neighbourhood of villages, where urine, &c., yields an abundant supply of organic nitrogen. In Bengal it is collected by a special caste, the 'Sorawallahs,' partly from the soil, partly from the surface of mud heaps, mud cottages, &c., by scraping off the uppermost layers which show a white efflorescence.

The following analyses show the composition of some Indian saltpetre earths:—

—	Tirhût (Stevenson)	Tirhût (J. Davy)	Ceylon (J.Davy)
Potassium nitrate .	0·7	8·3	2·4
Calcium nitrate .	0·9	3·7	—
Magnesium nitrate	—	—	0·7
Sodium sulphate .	2·7	—	—
Sodium chloride .	1·4	0·2	—
Calcium sulphate .	—	0·8	—
Magnesium sulphate	—	—	0·2
Calcium carbonate .	44·3	35·0	26·5
Insoluble in acids .	50·0	40·0	60·8
Water and organic substances .	—	12·0	9·4

Ganges mud, according to Warneford Lock, contains 8·3 p.c. potassium nitrate, and 3·7 p.c. calcium nitrate. This earth is lixiviated in earthenware dishes, or wooden boxes, or in pits dug in the ground and made tight by a clay puddle. The liquor is concentrated in iron pots, or sometimes only by solar heat, and a crop of very crude saltpetre is thus obtained. The mother-liquor is further evaporated to obtain common salt, and the last mother-liquor, which contains a large quantity of calcium and magnesium nitrate, is mostly run to waste. Occasionally a somewhat more rational process is pursued, by mixing wood-ashes with the saltpetre earth previous to lixiviation, or adding such ash to the solution during concentration; the potassium carbonate of the wood-ash then converts the earthy nitrates into potassium nitrate. The crude saltpetre, obtained from the clarified liquor by slow evaporation in earthenware pots, is called 'dhouah;' it contains from 45 to 70 p.c. KNO_3, and is re-crystallised by native merchants, who sell it in this state as 'kalmee.' The following analyses, by Tatlock, show the composition of some samples of Indian saltpetre:—

—	Bengal ordinary 1	Commercial 2	Bombay 1	Crude 2
Potassium nitrate	·51	89·36	72·46	36·06
Potassium sulphate	0·89	0·75	0·13	2·64
Potassium chloride	0·84	4·57	6·65	—
Sodium nitrate	—	—	—	0·26
Sodium chloride	0·20	0·31	17 41	47·43
Calcium sulphate	—	—	0·19	2·21
Magnesium nitrate	—	1·97	0·17	2·08
Insoluble	0·21	0·14	0·14	1·55
Water	1·35	2·90	2·85	7·95

A sample of the 'refuse salt' left behind on recrystallising the first crop of crude saltpetre, contained 8·83 K_2SO_4, 13·15 KNO_3, 21·14 KCl.

According to Ljubawin (Fischer's Jahresb. 1885, 262), there is a large deposit of saltpetre earth in the Khanat of Khiva, south-west of Fort Nukus, of the following composition:—

Soluble in water . .	27·89 p.c.
Souble in hydrochloric acid	17·14 ,,
Carbon dioxide . .	5·73 ,,
Insoluble in acids . .	48·42 ,,
	99·18 ,,

The portion soluble in water contains:—

KNO_3 . .	5·52 p.c.	$CaSO_4$ . .	3·25 p.c.
$NaNO_3$ . .	4·05 ,,	$MgSO_4$ . .	0·66 ,,
$Mg(NO_3)_2$.	1·04 ,,	Total nitrates	10·61 ,,
NaCl . .	12·90 ,,		

Saltpetre earths are found, and are worked by processes quite similar to those used in India, in some places in Persia, Egypt, Spain, Hungary (near Debreczin) and elsewhere.

An *artificial saltpetre earth* is, or formerly was, prepared in some European countries (Hungary, Switzerland, Sweden) by mixing a porous soil containing much calcium carbonate, with decaying animal substances; for instance, by preparing such a soil underneath the floor of stables where cattle and sheep are kept, the urine penetrates into the soil, and there undergoes the nitrification process. In Sweden, where formerly every landowner was obliged to furnish to Government a certain quantity of home-made saltpetre, all sorts of animal refuse was used up in this manner, in special 'saltpetre plantations.' About 100 tons per annum were made in Sweden in this way, but this process has been given up as unprofitable. In France, during the wars of the Revolution, when Indian saltpetre was inaccessible, that process was made compulsory by a decree of the Convention, and it is asserted that 2000 tons per annum were then made in this way; but there also the home manufacture had to be given up as soon as saltpetre could be imported from the East. Since the manufacture of saltpetre from nitrate of soda is making a severe competition even to Indian saltpetre, it seems quite hopeless to look to European sources for that substance; here the nitrogenous substances are better utilised for agricultural purposes.

Another kind of crude saltpetre, made from the mother-liquors from the working of 'caliche' for sodium nitrate, is sometimes sent to Europe from South America. It contains from 16 to 26 p.c. of potassium nitrate, 51 to 77 p.c. of sodium nitrate, 1 to 3 (exceptionally 16) p.c. of sodium chloride, and small quantities of sulphates and iodates. Its value is hardly greater than that of its equivalent of ordinary commercial sodium nitrate.

According to Sacc (Compt. rend. 99, 84), in Bolivia, near the village of Arané, East of Cochabamba, a large deposit has been found of the following average composition: 60·7 potassium nitrate, 30·7 borax, traces of common salt, and water, 8·6 organic matter. If this were confirmed, it would be very valuable indeed.

Refining of saltpetre. The East Indian saltpetre, before it can be used for the manufacture of gunpowder and other purposes, must be purified, especially from chlorides. This is done on a very large scale in England, France, and Germany (especially at Hamburg). The most usual is the French method. In an iron or copper pan 1050 kilos. saltpetre is dissolved in 600 litres of water at a gentle heat; the solution is brought to boiling heat, and another 1800 kilos. of saltpetre is dissolved in it. When employing these proportions with saltpetre containing about 20 p.c. of chlorides, the nitrate is dissolved completely, the chlorides but partially. The latter are fished out with a perforated ladle. If calcium or magnesium salts are present, potassium carbonate is added until a fairly alkaline reaction has been produced. The hot clear liquor is diluted with 300 litres of water, a solution of 1 kilo. glue in 20 litres of hot water is stirred into it, and the whole brought to boiling again. The glue combineswith the organic substances present forming a scum, which rises to the surface and is carefully removed. When no more scum rises to the surface, the liquor is allowed to settle for 24 hours, preventing any cooling down below 90°C., and the clear portion is run into flat copper coolers. As soon as the crystallisation begins, the liquid is constantly stirred, either by hand or better by machinery. Thus the potassium nitrate separates as minute, floury, crystals, which do not, like large crystals, inclose mother-liquor in hollow spaces. The crystal flour is drained; the mother-liquor (500 to 600 kilos.) is used over again in dissolving fresh saltpetre.

The small crystals must now be washed to remove all adhering mother-liquor. This is done in vessels provided with a perforated false bottom, covered with linen. When all liquor has drained off, the bottom tap is closed, cold water is sprinkled upon the salt by means of a rose, the whole is allowed to stand for some hours, and only then the liquor is run off. This is repeated several times, until the liquor shows next to no reaction for chloride. The last liquors are used in a new operation for the first washings. In this way the chlorides may be brought down to 0·005 p.c.

The drained crystal flour is dried in stoves or frames covered with canvas, or better on steam-heated pans, with mechanical stirring (just as they have been described for potassium chloride), and is mostly sold in this shape. Sometimes it is required in the shape of large crystals, which are very easily obtained by dissolving the flour in a small quantity of hot water and allowing the liquor to cool quietly and slowly. Exceptionally, it is fused into cakes or drops, which always contain a little nitrite (the 'sal prunellæ' or 'nitrum tabulatum' of pharmaceutical chemists).

II. *Manufacture of potassium nitrate from nitrate sodium.* 'Artificial saltpetre' was first made on a small scale by Longchamps and Anthon, with the aid of Chilean sodium nitrate and of potassium chloride, which, however, at that time was only obtainable from kelp, and was too expensive. When, in consequence of the increased demand for saltpetre during the Crimean war, especially in Russia, the manufacture of that substance from Chilean sodium nitrate became more remunerative, it was first carried out, in 1853, by Nöllner, Grüneberg, and others, with the aid of caustic potash and of Russian potassium carbonate; later on, more cheaply, with that of *vinasse cinder* ('schlempekohle,' *cf.* p. 359), which was used directly, without any separation of the salts. For this purpose sodium nitrate and a corresponding quantity of vinasse cinder were dissolved at the same time in boiling water; by the reaction $K_2CO_3+2NaNO_3=2KNO_3+Na_2CO_3$ anhydrous sodium carbonate was produced, which was fished out of the boiling liquid, together with the sodium carbonate originally present, and with the less soluble potassium salts, while the potassium nitrate remained dissolved at boiling heat and only crystallised out on cooling. The mother-liquor yields a mixture of about 53 parts NaCl, 31 Na_2CO_3, and 10 K_2SO_4, which is used by soap-makers (*cf.* Dingl. poly. J. 118, 200; 155, 418; 163, 314; 166, 75; Chem. Zentr. 1872, 491). This process has been given up long ago, principally because the separation of the salts is too difficult and the value of potassium carbonate is too great.

The separation of the substances is easier when *caustic potash* is employed, in which case the reaction produces potassium nitrate and caustic soda; the mixture can then be allowed to cool. The potassium nitrate is all but completely separated as fine crystals, and sodium hydroxide, with some impurities, remains in solution. By further concentrating this, solid caustic soda can be obtained. This process was carried out by Nöllner, Landmann, and Schnitzer (Dingl. poly. J. 117, 68; 162, 132) by adding lime to the boiling mixture of potassium carbonate and sodium nitrate until the alkali was causticised, whereupon the liquid was separated from the lime-mud, concentrated by evaporation, and allowed to crystallise. Much more rational than this was the process carried out at St. Helens in 1864 (*ibid.* 182, 385), decomposing potassium chloride by sulphuric acid, converting the potassium sulphate by Leblanc's process into a kind of black-ash, dissolving and causticising the caustic solution to sp.gr. 1·50, adding an equivalent quantity of sodium nitrate and allowing the potassium nitrate to crystallise by cooling. The mother-liquor was further concentrated, during which operation some salts were separated and fished out, and on cooling yielded a second crop of potassium nitrate; the second mother-liquor was worked up as caustic soda. This process does not seem to be worked now.

The process of Bolley (Wagner's J. 1860, 201; 1866. 227), converting sodium nitrate by means of barium chloride into barium nitrate, and converting this by potassium sulphate into barium sulphate ('permanent white') and potassium sulphate, is evidently not fit for general use, and can only pay in very exceptional circumstances.

The only process now in practical use is that of employing *potassium chloride*, originally proposed by Longchamps, and worked out by Anthon (since 1840, but more especially in 1858, Dingl. poly. J. 149, 39) in the shape in which it is now carried out. A theoretical study of the conditions of equilibrium between the reciprocal pairs of salts: KCl, $NaNO_3$ and $NaCl$, KNO_3, has been made by Meyerhoffer (Ber. 1904, 261, *et seq.*). The technical forms of the process have been described by Lunge (Dingl. poly. J. 182, 385) and Pick (*ibid.* 215, 222), and it is carried out in several modifications, the best of which will now be described.

Stassfurt 'muriate of potash,' containing not less than 80 p.c. KCl, and commercial sodium nitrate (95 p.c.), are brought together with mother-liquors from a previous operation and with the liquid obtained by washing the nitre bags. (The washed nitre bags, when dry, are exceedingly easily inflammable, and must be treated with the necessary caution.) The operation is performed in covered wrought-iron cylinders, 8 ft. diameter and 6½ ft. high, provided with a mechanical stirrer, a steam coil, and a tap for an open jet of steam; also with a 6-inch pipe in the cover, through which the steam given off in the cylinder is passed under the double bottom of the mother-liquor tank. The liquor is first concentrated by means of the steam coil to sp.gr. 1·53, adding a little oil in case of frothing, whereupon the materials are charged through the man-hole, first 3 or 3½ tons of sodium nitrate, then the corresponding quantity of potassium chloride, which is so calculated that a very slight excess of nitrate is present. The whole is boiled for half-an-hour to complete the decomposition, and is then run through a 4-inch tap on to the filter or strainer, consisting of a tank 8 by 8 by 5 feet, with a canvas-covered false bottom at a height of 4 ins. above the true bottom, and a steam-pipe between the two for keeping the liquor hot. Here the sodium chloride formed in the reaction

$$NaNO_3+KCl=KNO_3+NaCl,$$

which, owing to its relatively slight solubility in the hot concentrated solution, has been almost entirely precipitated in the solid form, is retained on the filter, while a liquor of sp.gr. 1·63 and a temperature of 95°C. runs off into the coolers. The common salt left on the filter is covered with hot mother-liquor, which is run off at a strength of 1·50 to 1·53, also into the coolers. The washing is then continued with liquors of decreasing strength, ultimately with pure water, until the salt contains only 0·6 to 0·9 p.c. of nitrate; at some works they go down to 0·25 p.c. The coolers are shallow iron vessels provided with either oscillating or revolving agitators, which can be lifted out of the liquid. The liquor is kept in agitation during the whole time of cooling, which, with a depth of 8 ins. in the vessels, ought to be finished in 30 to 36 hours. Sometimes this is hastened by a stream of water circulating on the outside of the vessel.

The mother-liquor, of sp.gr. 1·345–1·357, is run off into tanks provided with a double bottom, where it is heated by waste steam in order to be used over again at the first operation. Such mother-liquors are composed as follows. 100 parts by volume contain:

	a	*b*	*c*
Potassium nitrate .	29·40	25·5	26·4
Sodium chloride .	25·72	14·2	17·18
Sodium sulphate .	1·32	1·06	1·81
Magnesium chloride	2·10	6·2	8·19
Sodium nitrate .	—	19·6	7·19
Sodium iodide .	—	—	0·76

(*a*, sp.gr. 1·348 at 19°; *b*, sp.gr. 1·395 at 17·5°; *c*, remaining after working up 5000 tons of Chilean nitre).

The crude saltpetre flour, containing 7–9 p.c. NaCl, and 0·5–0·7 p.c. $MgCl_2$, is drained on one side of the cooler, and is washed with the liquor resulting from the washing of the refined saltpetre, with the use of the agitating gear, until the chloride has come down to 0·8–2 p.c. It is then refined by dissolving it in washings of the pure salt to sp.gr. 1·53–1·55, filtering as above, and running it into iron coolers; in doing this, a very small quantity of ultramarine is added, to neutralise the discolouration produced by a small quantity of iron. Here a mother-liquor of the following composition is produced:

	a	*b*
Potassium nitrate . .	20·91	23·4
Sodium nitrate . .	1·02	—
Sodium chloride . .	5·94	4·4
Sodium sulphate . .	0·12	—
Magnesium chloride . .	0·78	1·1

(*a*, sp.gr. 1·184 at 17°; *b*, sp.gr. 1·180 at 18·5°).

The crystals produced at the same time still contain 0·25 to 0·75 p.c. NaCl, and must be purified by washing them with water in copper-lined iron vessels, in the manner described above for potassium chloride; this produces a liquor of sp.gr. 1·075–1·083. The washed salt is drained, and is dried upon shallow, circular cast-iron pans, heated by means of internal steam channels; a revolving shaft moves the salt about by means of scrapers forced down by springs, and a conical roller at the same time crushes any lumps formed in drying. Each pan dries nearly 4 tons of nitrate in 24 hours. Unavoidably, some crusts are formed at the bottom, which must be knocked off once a day. The dried saltpetre need only be passed through a sieve to be ready for packing into casks.

It is asserted that, when German muriate of potash is employed, traces of magnesium chloride may remain in the saltpetre and render it deliquescent; this is to be counteracted by adding as much soda-ash as will throw down the magnesia. Muriate of potash made from kelp contains no magnesium chloride, but from 6 to 8 p.c. of sulphate, which does not decompose with nitrate as easily as the chloride. In Germany the above-mentioned drawback has never been found; nor can it be conceived that a mode of manufacture which actually brings down the total chloride to 0·01 p.c. should leave anything whatever of the extremely soluble magnesium chloride in the saltpetre.

The 'saltpetre salt'—that is, the impure sodium chloride formed in this manufacture—contains about 98 p.c. of NaCl in the dry state, with 0·25 to 0·9 KNO_3 and slight quantities of other matters. The nitrate makes it unfit for decomposing with sulphuric acid on account of the strong action on the iron pans; it is used for agricultural purposes, and for roasting the cinders from cupreous pyrites in the process of copper-extracting by the wet method.

Potassium arsenate KH_2AsO_4 (Macquer's salt) is manufactured by fusing together equal parts of potassium nitrate and white arsenic (arsenious oxide), dissolving the mass in water, and evaporating; on cooling the liquor the arsenate crystallises out in large, soluble, quadrate crystals, which do not deliquesce in the air. This salt is used in calico-printing as a substitute for cow-dung.

Potassium dichromate *v.* art. CHROMIUM.

Potassium cyanides, ferrocyanide and ferricyanide, *cf.* CYANIDES.

Potassium phosphate. The Stassfurter Chemische Fabrik vorm. Vorster and Grüneberg (D. R. P. 84954) decompose calcium phosphate with sodium sulphate, remove the precipitated gypsum, add to the solution of sodium phosphate the theoretically required quantity of potassium sulphate and cool down to +4°; Glauber's salt crystallises out and the solution contains primary potassium phosphate KH_2PO_4.

G. L.

POTATO, *Solanum tuberosum* (Linn.). This plant, a native of America, is grown for the sake of its underground tubers or thickened stems. These contain large stores of starch and other formative materials intended as nourishment for future plants. Each tuber has several 'eyes' which are compound buds, capable of producing one or more stalks. Many varieties are known, differing in colour, size, shape, and composition.

The following figures illustrate the variation in composition which has been observed:—

Water	Protein	Fat	Soluble carbo-hydrates	Crude fibre	Ash
68–82	0·5–3·5	0·05–0·80	12–26·5	0·3–1·4	0·4–1·5

The average composition (König) may be taken as—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
75·8	1·8	0·2	20·5	0·7	1·0

Of the total nitrogen, about half exists in non-proteid form, chiefly as asparagine, solanine, leucine, xanthine, and tyrosine. The proteids of the potato consist of a globulin—*tuberin*, soluble in dilute salt solution and showing coagulation on heating, incipient at about 60°, but not complete until 80°, and a proteose (Osborne and Campbell, J. Amer. Chem. Soc. 1896, 18, 575). The characteristic poisonous constituent of potatos is *solanine* $C_{52}H_{93}NO_{18}$, a crystalline substance melting at 244° and almost insoluble in ether and alcohol. It is decomposed by dilute HCl, yielding *solanidine* $C_{40}H_{61}NO_2$ (m.p. 191°), soluble in hot alcohol, and a sugar (Firbas, Monatsh. 1889, 10, 541). An amorphous substance—*solanëine* $C_{52}H_{83}NO_{13}$—which also yields solanidine when heated with hydrochloric acid, and which is apparently the anhydride of solanine—is also present in the shoots of the potato.

The sugars formed by the hydrolysis of solanine are dextrose and rhamnose, according to Zeisel and Wittmann (Ber. 1903, 36, 3554), whilst Votoček and Vondraček (*ibid.* 1903, 36, 4372) showed that galactose is also produced. This was confirmed by Wittmann (Monatsh. 1905, 26, 445), who also observed the formation of a dextro-rotatory sugar which he thought was probably a polysaccharide.

According to Wintgen (Zeitsch. Nahr. Genussm. 1906, 12, 113), the amount of solanine in potatos is very small, the highest and lowest amounts found being 0·1059 and 0·0172 parts per thousand. No increase in the amount was observed after prolonged storage, even in germinated potatos when the shoots were removed. He concludes that the amount of solanine is so small that no poisonous effect need be feared.

Nevertheless care should be taken that animals do not eat the young shoots of sprouted potatos, for they have been found to contain as much as 50 parts of solanine per thousand. Potatos, greened by the action of light, also may contain as much as 3 times the normal proportion of solanine (Kellner). According to Weil (Arch. Hygiene, 1900, 38, 330), certain bacteria induce the formation of solanine in potatos. Some samples of potatos contained 0·38 p.c. of solanine.

Of the nitrogen-free extract, starch constitutes the greatest portion, but sugar (varying from about 0·5 to 1·2 p.c.) and pentosans are also present. The starch occurs in large grains—the largest from 75μ to 110μ in length—of an oval, ovate, ellipsoidal or conchoidal outline, possessing a distinct hilum, generally situated in the narrow end of the grain and with well-marked, concentric striations. Potatos also contain small quantities of free acids, among which citric, succinic, and oxalic acids are probably the chief.

For many purposes, the commercial value of potatos depends upon their content of starch, and it is found that this may be deduced with sufficient accuracy (to about 1 p.c.) from a determination of the specific gravity of the tubers. This can be done by means of specially designed balances, capable of weighing about 5 kilos. of potatos in air and in water. According to tables calculated by Behrend, Marcker, and Morgen, the correlation between specific gravity of the tubers, proportion of total dry substance, and starch content, is as follows:—

Specific gravity	Percentage of dry matter	Percentage of starch
1·080	19·7	13·9
1·085	20·7	14·9
1·090	21·8	16·0
1·095	22·9	17·1
1·100	24·0	18·2
1·105	25·0	19·2
1·110	26·1	20·3
1·115	27·2	21·4
1·120	28·3	22·5
1·125	29·3	23·5
1·130	30·4	24·6
1·135	31·5	25·7
1·140	32·5	26·7
1·145	33·6	27·8
1·150	34·7	28·9

Obviously such a table can only claim appromixate accuracy since the proportion of starch to other solid matter is variable in different tubers.

Balland (Compt. rend. 1897, 125, 429) found, as the result of the examination of a large number of varieties of potatos grown in France, the following:—

	Weight of tuber grms.	Water	N-compounds	Fat	Starch and sugar	Fibre	Ash
Maximum	420·0	80·0	2·8	0·14	29·9	0·7	1·2
Minimum	23·0	66·1	1·4	0·04	15·6	0·4	0·4

The ash generally contains traces of manganese. The acidity varied from 0·07 to 0·25 p.c.

Forfang (Bied. Zentr. 1904, 33, 392) found, as the average of ten analyses of potatos grown in West Norway—

Water 75·6 p.c., total dry matter 24·4, starch 15·2, sugar 2·2, crude fibre 0·7, furfuroids 0·7, total N 0·4, fat 0·04, and ash 1·0 p.c.

Coudon and Bussard (Compt. rend. 1897, 125, 43) have examined the separate portions of potatos. They find that after the removal of the skin, there are three distinct layers, differing in composition—the cortical layer containing the highest proportion of starch and the lowest proportion of water and nitrogenous matter—the external medullary layer of intermediate composition and the internal medullary layer which is richest in nitrogenous matter and water and poorest in starch. The proportion of starch in the cortical layer may be twice as great as in the innermost layer, whilst, in the latter, the amount of nitrogenous matter may be 28 p.c. higher than in the cortical layer. They state that the culinary value of potatos is directly proportional to the quantity of nitrogenous matter and inversely proportional to the amount of starch present, and that it may be measured by the ratio between these quantities. The power of the tubers to retain their shape and size when boiled in water is determined by the proteids present and is not dependent upon the proportion or size of the starch grains or the amount of pectin substances present. The resistance to swelling up when boiled is measured by the ratio, proteid : starch, which in good varieties varies between 1 : 14 and 1 : 8·6, while in the varieties which disintegrate most it is 1 : 6 or even 1 : 4.

They conclude that for culinary purposes, the aim should be to cultivate varieties with a thin cortical layer and therefore poor in starch, whilst for industrial purposes, varieties with a thick cortical layer and a high content of starch are to be preferred.

New varieties of potatos are continually being produced, for some of which great advantages are claimed.

In 1901, a wild plant growing in Uruguay, which was first described in 1767 by Commerson, was brought to Europe by Heckel. By cultivation, an edible tuber, equal to the ordinary potato, has been obtained, which it is claimed is immune to ordinary potato diseases, more resistant to frost, and capable of yielding enormous crops. This plant is known as *Solanum Commersonii* (Dun.) and is characterised by the large number of aerial tubers which it produces, in addition to its subterranean ones (Labergerie. Bied. Zentr. 1905, 34, 616).

The ash of potatos, according to Wolff, contains on the average—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
60·3	2·6	2·6	4·7	1·2	17·3	6·4	2·0	3·0

Potatos are extensively used as human food, as food for farm animals (best after boiling or steaming), and industrially, as a source of starch (*q.v.*), alcohol and fusel oil (*q.v.*).

As a food for animals, potatos are used raw, steamed, as silage, or, recently, dried. The following figures (Kellner) show the composition of these various forms:—

—	Water	Protein	Fat	N-free extract	Fibre	Ash
Raw, medium	75·0	2·1	0·1	21·0	0·7	1·1
,, watery	83·0	1·6	0·1	13·9	0·6	0·8
,, dry	74·0	2·1	0·1	21·9	0·8	1·1
Steamed	66·5	1·5	0·1	30·1	0·8	1·0
Raw, as silage	73·5	2·2	0·5	21·7	0·7	1·4
Dried	12·0	7·4	0·4	74·0	2·3	3·9

The haulms and 'apples' (fruit) of potatos contain, usually, sufficient solanine to render them poisonous. They should not be used as food for animals.

Potatos grow best in deep soils, well drained, free from acidity, and well supplied with potash and nitrogen.

For examples of the efficiency of spraying potato plants with copper compounds as a preventative of blight, *v.* Leaflet 14 of the Dept. of Agric. and Techn. Instruction for Ireland.

H. I.

POTATO OIL *v.* FUSEL OIL.

POTATO STARCH *v.* STARCH.

POTTERY and **PORCELAIN.** The term 'pottery' is a very elastic one, being commonly used to indicate any article fashioned of clay (or of a mixture of clays and other mineral substances), and hardened by the application of fire. In this sense the term includes all kinds of crockeryware and such common articles as flooring and roofing tiles, drain-pipes, bricks, and crucibles; nor is there any reason why this comprehensiveness should be curtailed, for though a vase of Sèvres china and a drain-pipe are widely different when finished, they come equally well within the scope of our definition, and their production depends upon the application of exactly similar principles; the superior result obtained in the one case being mainly the result of superior elaboration and care.

Potteryware of every kind is usually divided into two great classes—

1. Simple or unglazed, such as flooring or roofing tiles, bricks, terra-cotta, primitive pottery, &c.

2. Composite or glazed, such as the ordinary forms of porcelain, earthenware, or stoneware used for domestic purposes.

This distinction is an arbitrary one, for almost every kind of pottery is capable of existing in both forms and of serving some useful purpose in each of them. The distinction is of value in so far as it helps us toward an easier conception of the term 'body' or 'paste' and 'enamel' or 'glaze'; the body being the stuff or substance of which the article is first fashioned or shaped and the glaze or enamel an external covering resulting from the formation of a vitrified coating on the body, to render it impervious to liquids or to serve æsthetically as decoration. A clear conception, therefore, of the various pottery bodies—of the processes by which they are prepared and of their relationship to each other—forms the simplest starting-point from which to review the science of the potter.

The foundation of every pottery body, without exception, is one or other of the natural clays, for the bare possibility of a pot, as we know it, results from two properties which the clays alone possess in any marked degree, viz. the property of being kneadable while moist into almost any required shape (what we call plasticity); and, secondly, the property of becoming dense, hard, and durable when fired (*see* art. CLAY). While, however, the possession of these properties renders the use of some form of clay unavoidable further manufacturing qualities are required in a good body which can only be secured by the addition of other materials. Thus articles made from a natural plastic clay are apt to crack in drying, owing to the tenacity with which such clays retain the water added in working; in firing they are apt to soften a little, especially if the clay contains much iron or lime, and so lose their shape. These defects necessitate the admixture of sand, ground flint, or other aplastic or hardening materials, so as to make the body more open or less retentive of water, or to render it less liable to sink, in the firing, from partial fusion. Again, in some classes of pottery translucence is a necessary quality of the fired ware and this can only be secured by the due admixture of selected clays with suitable fusible materials, which vitrify when submitted to the heat of the pottery oven and, enveloping the minute particles of clay with which they are mixed, produce a semi-transparent material.

All the substances commonly used in the composition of pottery bodies may be divided into three classes according to their primary functions:—

1. Plastic materials: all the varieties of clay and marl.

2. Hardening or aplastic materials (Fr. *dégraissantes*): flint, sand, quartz, ground pitchers, &c.

3. Fusible materials: felspar, china stone, bone ash, lime, gypsum, barytes, artificial fritts, &c.

The object of the potter is to select from the materials at his disposal such as will enable him to produce a suitable body under his conditions of working and firing; for it must be borne in mind that one and the same substance may play a different *rôle* in the body, according to the method of manufacture or temperature of firing. Thus, the addition of quartz to the body mixture of certain European porcelains produces a mass which matures at a lower temperature than the mixtures of china clay and felspar that were formerly used. Every form of pottery must be regarded as a mass of mixed silicates of indefinite composition, and the practical result depends both on the composition of the mass and the degree of chemical rearrangement that has taken place during the firing. In no cases are the chemical changes pushed to completion, or we should have a fused slag or glass, but the reactions are arrested at some arbitrary stage which practice has shown to be advisable. Chemical analysis may prove that a pottery body contains certain proportions of silica, alumina, &c., but the potter's business is to prepare such mixtures as possess sufficient plasticity and tenacity to enable articles to be fashioned and dried without undue loss, and capable, when properly fired, of yielding wares possessing the requisite durability, infusibility, colour, texture, &c.

The current classification of pottery into earthenware, stoneware, porcelain, &c., is thoroughly unscientific, for the distinctions on which it is based, such as colour, hardness and translucence, are mainly accidental and are often due quite as much to the methods of manufacture and the firing temperature as to inherent differences in the bodies themselves. It is impossible in the present state of our knowledge to draw any hard-and-fast line between the different classes of pottery; but perhaps the following classification, designed to bring out the natural relationships of the body mixtures, has as much to recommend it as any:—

First class. Bodies containing only plastic materials, or a mixture of plastic and hardening materials. It is impossible to separate this into two classes, as the question whether any hardening material must be added depends entirely upon the nature of the particular clay. In this class the following products would be included: bricks, flooring and roofing tiles, ordinary stonewares, and the common red and brown wares of all countries. The fired body is always opaque, moderately hard, and generally strongly coloured—red, grey, or buff.

Second class. Bodies containing plastic, hardening, and fusible materials. The bodies of this class naturally cover a wide range according to the proportion in which the three classes of material enter into their composition. The fired products are hard, dense, generally opaque and white or pale in colour. All the better kinds of English earthenware, stoneware, granite and mortar bodies would be included.

Third class. Bodies containing plastic and fusible materials, mainly. The most refined species of pottery—such as hard porcelain, soft porcelain (both natural and artificial), parian, jasper, &c.—belong to this class. The fired bodies are very hard, durable and translucent, and, unless stained by added colouring oxides, are white or creamy in colour.

Preparation of the body. In the preparation of all working mixtures for the potters' use the first object to be aimed at is perfect homogeneity, and the more complex the body the more important does attention to this point become. For bodies of the first class it is usually sufficient to remove stones and other hard foreign matters and then pass the material through a pug-mill or mortar-mill to secure sufficient uniformity (*see* art. CLAY); but for bodies belonging to the second and third classes, where articles of high finish and mechanical perfection of shape are required, it is necessary that all the materials be reduced to a very fine state of sub-division in order to bring about their intimate admixture. The processes for this purpose are much the same for all classes of body mixtures, and it will only be necessary to describe the methods used in the preparation of English earthenware (in many respects the most complex of all) as they are quite suitable, with slight modifications in detail, for the preparation of all other bodies.

The substances used for this particular body are: ball clay from Devon or Dorset, china clay from Devon or Cornwall, china stone from Cornwall, and boulder flints from the sea beaches of Dieppe, Treport, &c. The clays used vary greatly in plasticity, and the proportion of stone or flint with which they are mixed depends largely upon this quality of the clay. The proportions used for the average cream-colour body are: ball clay, 50 p.c.; china clay, 10 p.c.; flint, 37 p.c.; china stone, 3 p.c. The clays are beaten up to a pulp with water in a blunger or iron chest in which a shaft carrying broad-bladed knives is rapidly rotated. This fluid paste is known technically as 'slip.'

The flint and stone must be reduced to impalpable powders, in order that their particles may be uniformly diffused among the particles of clay in the slip. The flints are first calcined, usually in specially constructed kilns; this calcination having rendered them white and friable, the nodules are then broken into coarse lumps in an ordinary stone-crushing machine and finally charged on to a pan similar to the one shown in section in Fig. 1.

The pan is built up from the floor, either with iron sides or with wooden staves strongly hooped together. The bed or bottom (*d*, Fig. 1) is a pavement of chert stones from 8 to 16 ins. thick, according to the size of the pan. Over the face of this pavement large blocks of chert, weighing a ton and over in the case of large pans, are driven round and round by the arms (*c*) fixed on a vertical shaft (*a*). The fragments of calcined flint, or other material to be ground, are charged on to this pavement (*d*), a little water is run in and a grinding of longer or shorter duration, according to the weight of the grinding stones, suffices to reduce the material to fine powder in suspension in water. This form of pan is extensively used for the grinding of all classes of pottery materials, such as flint, stone, felspar, glaze, &c., that are required in a state of powder. The stones of the pavement and the runners are, of course, worn away; hence it is advisable to have them of some substance whose introduction into the body in small quantities will not cause any serious disturbance of its properties. Chert paving stones and runners are obtained in the districts round Mold and Chirk in North Wales, from the Bakewell and Bradwell districts of North Derbyshire, and blocks of massive quartzite are also quarried in the neighbourhood of Oban, in Achill Island and in the vicinity of Cherbourg. In the pans for grinding china-stone, blocks of hard china-stone are often used both as pavers and runners. A pan of this description, 12 ft. in diameter, and carrying a load of from 5 to 6 tons of runners, should grind 1 ton of calcined flints in 12 hours. In recent years grinding cylinders of various types have to some extent replaced this type of grinding pan. An iron cylinder, lined with blocks of quartzite, stoneware, or porcelain, and provided with a manhole for the introduction and removal of the charge, is mounted on bearings so that it can be rotated. The material to be ground (flint, felspar, fritt, &c.) is charged into the cylinder in a coarse powder, such as is obtained by passing it through a crusher or edge-runner pan and a charge of flint pebbles or other suitable pulverising material is added. The manhole is then tightly closed and the cylinder rotated, when the moving charge of pebbles and material gradually reduces the latter to an impalpable powder. The material can either be ground dry or, preferably in most cases, with water. (For discussion of 'dry' and 'wet' grinding and of 'pan' and 'cylinder' grinding, *see* various papers in The Transactions of the English Ceramic Society, and especially Studies on Cylinder Grinding, Mellor, Trans. Eng. Cer. Soc., 9, 50 *et seq.*)

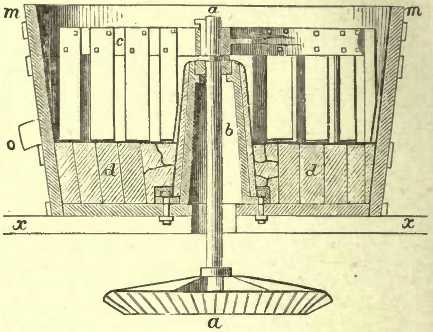


FIG. 1.—GRINDING PAN.

x. Floor line. *m*. Pan sides. *d*. Pavement of chert. *a*. Driving shaft, working in centre tub *b*, and carrying arms *c* which drive large blocks of chert over the face of the pavement *d*.

To avoid waste of time and power in the 'wet' grinding of such materials, a process of elutriation is used. It is obvious that when a charge of material is ground the efficient work must be completed in a certain time and further grinding is, largely, wasted. At this stage the material is run off the grinding pan or cylinder in varying grades of fineness, mixed with two or three times its bulk of water and thoroughly agitated. The mixture is allowed to settle, and, by the simple process of drawing off successive fractions from a settling tank (known as a wash-tub), the finer particles are drawn away for use and the coarse particles are collected as residue and returned for regrinding. The question of the size of particles of such materials as flint, quartz, &c., is of great technical importance (*see* papers in The Transactions of the English Ceramic Society and The American Ceramic Society).

Having thus obtained all the materials in a fine state of sub-division and in suspension in water, each is run into a separate vat, the cubic contents of which are known. The specific gravity of each of the 'slop' liquids is ascertained and the proper quantities are mixed in a big vat or blending ark and thoroughly agitated. Such a mixture is known as 'slip.' This method of slop blending—at best a rough volumetric one—though in general use, needs very careful supervision in order to obtain accurate results. Alternatively, the ground and dried materials are each separately weighed and then agitated together in water. The difficulty of this method, which at first sight looks simpler, is to obtain the materials in a state of consistent dryness, for clays which are apparently dry retain 2 or 3 p.c. of water. In very precise work the latter method is preferable; on the manufacturing scale the former is sufficiently accurate.

When the materials have been made into slip they are carefully sifted through fine sieves of brass, silk, or phosphor-bronze to remove all coarse particles, dirt, &c., and then finally 'magneted' to remove any particles of metallic iron, or of magnetisable iron compounds, which may have come in by way of the materials or from the machinery, and which, if left in the paste, produce black specks, a quite unsightly disfigurement in white bodies. In this country the 'magneting' is done by running the slip through a box or spout containing a number of horseshoe magnets suspended so that they nearly touch the bottom; or electro-magnets are used. Twenty years ago such methods were in their infancy, but during that time many ingenious devices for sieving and electro-magneting have been invented for dealing with potters' materials at various stages of their preparation. The slip mixture, thus cleansed, is in condition to be made into potters' clay. Two methods of doing this are in widespread use. The older method is one of evaporation, in which the slip is run into shallow brickwork tanks (slip-kilns) to a depth of from 6 to 8 ins., and then dried to the proper consistency by fires burnt under the tanks or by coils of steam-pipes. This process is now only used where small quantities are to be operated on, where many different bodies are made, or where the nature of the mixture is such as to render the removal of small amounts of soluble salts undesirable. Clay made in this way must be carefully beaten together to render it of uniform consistency, for it is liable to contain hard lumps that have been burnt from contact with the brickwork; the process, too, is slow, and therefore quite inadequate for the production of the large quantities of clay required in the great pottery works of England and other countries. The method now adopted in all works where large quantities of clay are required is one of filtration under pressure. The slip is delivered, by force-pumps working at pressures up to about 76 lbs. on the square inch, into strong canvas bags supported between fluted wooden or iron trays securely clamped together. The bags expand a little until they fill the space between each pair of trays, and then act as filters, the water being driven through the pores of the cloth and a mass of plastic clay left behind. The time taken up in this process depends upon the nature of the body; bodies like those of porcelain, granite-ware, &c., which contain only a small proportion of plastic material part with their added water readily; those used for many varieties of earthenware, which contain a large proportion of plastic clay, retain their water more obstinately and take a longer time to attain the right consistency. The potters' clay, as it is delivered from the filter-press, is always harder on the outside of the cake than on the inside and it is either thoroughly beaten together or put through a pug-mill or rolling machine to render it uniform in consistency and free it from air-bubbles.

Some reference must be made to the obscure phenomena connected with what is known as the 'ageing' of prepared clays. Centuries of practical experience have shown that such mixtures improve in plasticity and working properties if they are kept for a considerable period and watered, beaten, and turned over occasionally. The probable explanation of this long-recognised fact is to be found in the modern view that clay is a colloidal substance. It has been fairly well established that the plasticity of a clay or clay mixture is determined by the amount and nature of its colloids. The action of relatively small amounts of acid or alkaline substances on clay is thus explicable; likewise the fact that the addition of certain colloids—such as glue, size, or soap in ancient practice and tannic acid or tannates in modern work—has proved of value in improving the working properties of a clay mass. Another practical outcome of the action of dilute alkalis on clays will be referred to in connection with the latest methods of casting pottery (*q.v.*).

The body being ready, then, for the hands of the potter, some consideration must be bestowed on the methods of shaping the desired articles from it, for these methods vary both with the shape and the size of the article and with the nature of the body. For round articles and with plastic mixtures a very old process, that of 'throwing on the wheel'—is generally adopted; but for articles of oval or irregular shape, or with bodies of slight plasticity, other methods must be used and of these the most important are pressing and casting.

Pressing is a technical term applied to two distinct processes: (*a*) plastic pressing, in which the article is made from moist clay; (*b*) dry pressing, in which the article is stamped out of clay dust. In plastic pressing the clay is beaten or rolled out into a thin cake or 'bat,' which is then pressed by the workman into moulds of plaster of Paris or baked clay (exceptionally of sulphur or metal), which are generally made in sections so as to be readily taken to pieces. When each section of the mould has had a bat of clay applied to it and rubbed down into all its lines and indentations, the portions are fitted together, tightly strapped up, and the seams or joints are smoothed down so that the clay forms one piece inside the mould. On standing, the clay dries a little so that it contracts slightly and thus releases itself from the mould; when it is sufficiently hard to bear handling the mould is taken apart and the piece removed; its seams and edges are trimmed down and sponged smooth and it is put to dry in a hot-air stove, preparatory to firing. Many articles of pottery are now made, commercially, by pressing plastic clay mixtures in a die or through a 'template' of the required shape by mechanical power. This process is known as 'compression.' It is largely used for the manufacture of drain or sewer-pipes, or, with suitable modifications, for bricks, roofing tiles, building blocks, crucibles and similar articles. The enormous quantities of tiles used in the internal decoration of buildings are prepared by the 'dry' pressing process. The body, after a careful preparation as detailed above, is taken from the filter press, dried, and then ground to powder in a disintegrator or between rollers or mill-stones. This powder or clay-dust is slightly damped so that if a handful of it is squeezed it adheres loosely together. It is filled into a metal mould, a die is forced down upon it by hand- or mechanical-power and the tile is thus stamped from the clay dust. Such a tile possesses sufficient adhesion to bear the handling necessary to fire it and when fired it becomes hard and sonorous, though not quite so hard or durable as a tile made from clay by the old plastic process.

Casting. The third method in general use for the fabrication of pottery articles is the simplest of all methods and is mostly used for those mixtures which do not yield a very plastic body, such as those required for the ordinary porcelains and parians. The mixed slip is not made into clay, but, after being got to such density that a pint of the fluid mixture weighs about 30 oz., it is poured into moulds made of plaster of Paris. The plaster, being porous, absorbs the water from the 'slip,' and a thin coating of clay is deposited on the inside of the plaster mould. When this coating is of sufficient thickness the remaining slip is poured out and the mould and its clay cast are set aside to drain. After the superfluous slip has drained away the mould is placed in a hot-air stove; the cast shrinks away from the mould and can then be drawn out (or the sections of the mould are removed from it), smoothed off, thoroughly dried, and the cast article is ready for the firing process. For an account of the application of compressed air, &c., to enable large pieces of porcelain to be cast, *see* Auscher, 'Technologie de la Céramique,' pp. 158–159.

A striking instance of the application of scientific method to ancient practice is shown in the most recent developments of the casting process. The method of casting pottery seems to have been invented by the Staffordshire potters of the period 1740–1750 and they soon learnt that the addition of a dilute alkaline solution such as that of sodium carbonate, enabled them to 'cast' mixtures that were otherwise impracticable. In 1891, Goetz was granted a German patent for this application (D. R. P. 76247, 1891), and this was hailed as a remarkable discovery though it had long been known in England and France. The method has, however, become of great practical importance, for the addition of dilute solutions of alkaline substances (soda, potash, waterglass, &c.) to an ordinary clay mixture enables the potter to use a clay slip at 36 oz. to the pint, containing, therefore, only about 30 p.c. of water instead of about 50 p.c. of water contained in slip at 30 oz. to the pint. This slip pours better and is freer from bubbles of air than ordinary slip and the method is now extensively used in the manufacture of large sanitary pieces, glass-pots, building blocks, saggers, &c., for it can be used either with ordinary clay mixtures or with those to which coarse materials, such as 'grog,' ground pitcher, &c., have been added. Its use also allows the fabrication of tea-pots, jugs and other intricate shapes in one piece where, formerly, the articles had to be made in three or four separate moulds. This action of dilute alkaline solutions is explained by supposing that the clay colloids have been changed from 'gel' to 'sol' (*see* J. W. Mellor, &c., Trans. Eng. Cer. Soc. 1906–1907, p. 161 *et seq.*).

Though applied with slight difference of detail to suit different bodies, and with the introduction of much machinery for the saving of labour, these three methods of throwing, pressing and casting comprise in principle all the methods used in the shaping of pottery. (For details of the processes in actual use, *v.* works mentioned in the bibliography.)

The following table exhibits in percentages the composition of the most important bodies in general use:—

Sèvres Porcelain (hard Porcelain): kaolin 48, felspathetic sand, 48, chalk 4.
Berlin Porcelain (hard porcelain): kaolin 75, felspar 25.
Meissen Porcelain (hard porcelain): kaolin 73, felspar 25, ground porcelain pitchers 2.
Vienna Porcelain (hard porcelain): kaolin 72, felspar 12, quartz 12, gypsum 4.
English Bone China: china clay 25, china stone 25, bone ash 50.
English Cream-coloured Earthenware: ball clay 50, china clay 10, flint 35, stone 5.
English White Earthenware: ball clay 25, china clay 32, flint 34, stone 8 oxide of cobalt 0·05.
English White Tile Body: ball clay 28, china clay 28, flint 40, stone 4.
English Granite Ware: ball clay 25, china clay 25, flint 40, stone 10, oxide of cobalt 0·08.
English Terra-cotta: red marl 90, flint 5, Cornish stone 5.
English Parian: china clay 36, felspar 64.
English Mortar Body: ball clay 25, china clay 20, stone 55.
English Evaporating Pan Clay: ball clay 25, china clay 14, stone 46, flint 15.
English Fine White Stoneware: ball clay 25, china clay 20, flint 10, stone 45, oxide of cobalt 0·02.
English Black Clay: red marl 75, oxide of manganese (MnO_2) 6, calcined clay ironstone 19.
French Silicious Faience: china clay 24, chalk 24, flint or sand 48, fritt 4.
Fritt for above: sand 85, potassium carbonate 7, sodium bicarbonate 3, whiting 5.

French Tile Body: ball clay 25, chalk 25, sand 15, crushed firebrick 35.

These mixtures are extensively used, but, as already said, the potter of every country must use in practice such clays and other substances as are readily procurable to meet his particular requirements. The history of pottery shows how much the potters of every time and country have been influenced in their doings by the materials at their command. How profoundly the final result is influenced by methods of treatment may be seen from the following table, where the chemical composition of the most important modern species of pottery is shown:—

—	Silica	Alumina	Oxide of Iron	Lime and Magnesia	Alkalis
	P.c.	P.c.	P.c.	P.c.	P.c.
Ordinary stonewares . .	68–75	20–25	2–10	1–2	2–5
Fine white stonewares . .	70–75	20–25	0·2–1	0·5–2·5	3–5
English earthenwares . .	66–75	17–28	0·1–1·5	0·5–2	2–3
Hard porcelains.	60–75	19–33	0·1–1	0·5–1	2·5–5

The old view of the classification of pottery bodies seemed to imply that, given a certain percentage of silica, alumina, &c., we had a complete explanation of the differences between earthenware, stoneware, and porcelain. The above table, which represents the reduction of hundreds of analyses, together with a great mass of other facts, serves to show that the chemical composition is of minor importance compared with (*a*) the chemical and physical constitution of the materials used; (*b*) the amount of rearrangement that the conditions of firing and its final temperature ultimately produce.[1]

Firing of the body. The firing of the ware is one of the most important branches of the potter's business, for the durability and economic value of any kind of pottery largely depend upon this factor. Each mixture requires a different method of firing, or a different degree of heat, to yield the best result. As a general rule, bodies of the first class do not require so much heat as those of the second class, nor those of the second so high a temperature as those of the third class. A clear red heat (800°–900°) is quite sufficient, for instance, for the burning of ordinary bricks; the bodies of the second class require a white heat (1150°–1250°); whilst of the bodies included in the third class, English bone china requires about 1250°, and hard porcelain requires still higher temperatures (1300°–1500°), varying according to the composition.

Bricks, common tiles, drain-pipes and other coarse pottery are exposed directly to the flames and may, indeed, be burnt in heaps or clamps, though burning in kilns or ovens is now largely superseding the old wasteful method of burning in the open. For the finer bodies, however, such as those of the second and third classes given above, direct contact with the flames, except when the articles are to receive a salt-glaze, is generally inadmissible and such articles are therefore inclosed, or carefully packed, in fireclay boxes known as saggers (Fr. *cazettes*), which are piled one upon another—each pile of saggers being called a 'bung'—in a large chamber built of firebrick. Such a chamber forms a kind of vertical reverberatory furnace and the flames play directly into it. The particular form of furnace used, the methods of firing, and the sequence of operations are so different in the case of hard porcelain from those employed with other species of pottery that they demand a separate notice.

Hard porcelain is one of the most distinct types of pottery, but owing to the lack of sufficiently refractory fireclay and to various other causes, many of them economic, its manufacture has never obtained a permanent foothold in this country. In various European countries, as well as in China and Japan, it is extensively manufactured and in the table given above will be found the composition of the bodies used at the imperial factories of various countries. From the composition of these mixtures it is obvious that they can possess only a relatively low degree of plasticity and the manufacture of large and elaborate pieces becomes difficult and costly. Technically, the most distinctive feature of this form of pottery, whether we are dealing with the products of Europe or the Far East, lies in the fact that the body and glaze are fired together at a high temperature. In other important species of pottery, except salt-glazed or once-fired wares where the temperature is not so high, the body is first fired to a high temperature, which produces durable 'biscuit' pottery, and then, at a subsequent operation, a coating of fusible materials is melted over the surface. The fine, white earthenwares of English manufacture have, practically, the same ultimate chemical composition as porcelain (*v.* table above), but the firing temperature is not sufficient to bring about the molecular re-arrangement that we may call 'porcelainisation,' though it is quite sufficient to produce a distinct species of pottery possessing some useful qualities that porcelain lacks. In hard porcelain the manufacturer must use mixtures and processes by means of which the body will 'porcelainise' and the glaze mature at one and the same temperature (*v.* Burton, W., Porcelain, &c., 1906, chap. i. *et seq.*). A pottery mixture becomes 'porcelainised,' probably when the chemical and molecular rearrangements have proceeded so far towards fusion that, instead of an indefinite mixture of aluminates and silicates with free silica, a stage is reached in which definite silicates are formed and the preponderance of certain crystalline or micro-crystalline compounds confers on the fired mass optical and other physical properties which have, for centuries, been recognised as distinguishing the porcelains (very indefinitely) from other kinds of pottery.

When the articles have been shaped, they are air-dried (Chinese practice), or are fired to a comparatively low heat, *feu dêgourdi* 700°–900°, (Japanese and European practice) in a globe or chamber (B, Fig. 2) placed over the oven proper and heated by the waste heat from it. By this latter operation the articles are completely dehydrated and rendered hard enough to take a coat of glaze with less risk of breaking. The glaze consists generally of felspathic minerals similar to those used in compounding the body, or of mixtures of felspar, quartz, &c. (*v. Glazes, infra*), ground to fine powder and held in suspension in water. The article, whether dehydrated or air-dried, is dipped in the mixture, or the glaze is pencilled or blown on to it, and, on drying, a coating of fine glaze-powder is left on the piece. The pieces are then placed in saggers of the most refractory fire-clay, and elaborate precautions are taken to support them so that they shall not touch each other or the sides of the saggers; they are also propped and supported from certain points so as to diminish the risk of sinking out of shape in the firing owing to the partial fusion of the body which takes place. The saggers of ware are then placed in the oven (A., Fig. 2) in piles or bungs until the oven is suitably filled. The doorway D is bricked up and a fire is started in each of the mouths C, of which there are four to eight or ten at equal distances round the oven. In some cases two or more chambers are built above each other, and the gases from the first are conducted through the others in such a way that when the first oven or chamber is sufficiently fired the one above it is about half fired, so that a much smaller quantity of fuel is needed to complete the burning. The form shown in Fig. 2 is that generally used in Limoges, the great seat of the French porcelain industry. Wood was commonly used as fuel until recent times because of its long, clear flame; but nowadays coal or some gaseous fuel is used (*see* below). The firing is allowed to proceed slowly for 12 to 20 hours, so that the contained and combined water may be expelled from the body by slow and gradual stages. When the temperature reaches 600°–700° all danger of cracking or rupture of the pieces from this cause ceases, and the temperature can be raised more rapidly. Beyond this point, the silicates begin to fuse and react upon each other, and the increments of temperature must be gradual and regular until the final point is reached. Then the temperature must be maintained in a state of equilibrium for a sufficient period to allow the new compounds to mature. The firing period varies from 60 to 120 hours, after which the fire-mouths are closed and the oven and its contents are allowed to cool slowly.

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[1] It must not be assumed that all pottery bodies have compositions which lie between these figures; these are only typical of large and important groups.

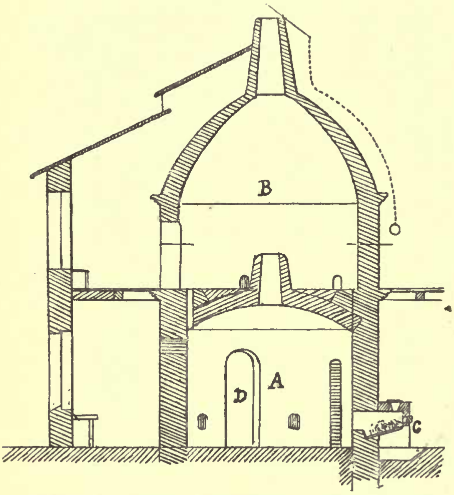
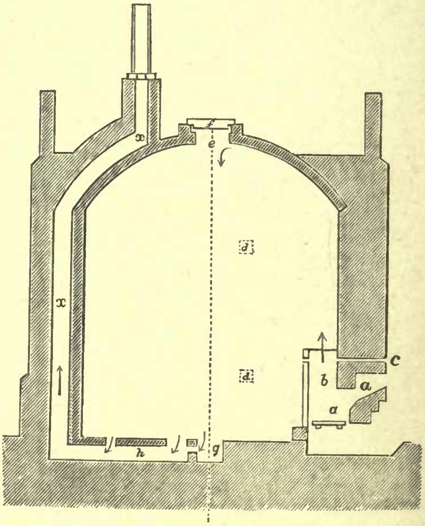


Fig. 2.—Oven for Hard Porcelain.

A. Oven proper. B. Globe where the ware is hardened before glazing. C. Mouth or fireplace. D. Door.

Other bodies. With all other species of pottery—except those which are so vitrifiable as to need no glaze, becoming of themselves impervious to liquids, and those which are fired and glazed at one operation without 'porcelainisation'—there are two distinct firings of the ware. In the first, known as the biscuit firing, the clay article is very strongly heated, becoming hard, compact and sonorous, and though remaining porous, it may be so durable as to serve many useful purposes. To render it impervious to liquids, or for various decorative purposes, this once-fired pottery, known as 'biscuit' or 'bisque,' receives a coating of glaze material and is refired at a sufficiently high temperature to vitrify this glaze. This second fire is known as the 'glost' fire, and is always of less intensity than the 'biscuit' fire. The ovens commonly used for biscuit-firing are shown in Figs. 3 and 4.



Across one of the chimneys. Across one of the mouths.

Fig. 3.—Vertical Section of Minton's Patent Oven.

a. Mouth. *b*. Bag or short chimney into oven. *c*. Peep-hole. *d*. Holes for drawing trials. *e*. Crown-hole, closed during firing by damper *f*. *g*. Well-hole, communicating with flues *h*, which open into chimneys *x* in the walls of oven.

The form of oven shown in Fig. 3, above, and known as the down-draught oven, is an improvement on the older form (Fig. 4). Here there are no flues running from the mouths under the floor of the oven, but all the flame plays into the firing chamber by the short, upright 'bags' or chimneys (*b*). The flames go up the side of the oven to the roof or crown; but, as the damper (*f*) is closed during the firing, the flame is reverberated down through the central portions of the oven, and the smoke and waste gases are drawn out through the well-hole (g) and the flues (h), which open into the chimneys (x) inclosed in the wall of the oven in the space between each pair of mouths. The heat is more evenly distributed in this form of oven than in the old form (shown in Fig. 4 and described below); there is a larger yield of well-fired pottery from it, and the same quantity of pottery is fired with a smaller consumption of coal. This form of oven is, however, more costly to build, and unless the proportion of air space in mouths, chimney, and oven is carefully regulated, one portion of the firing chamber may be heated sufficiently while another part may be relatively cold. The ovens used in this country range from 12 to 20 ft. in internal diameter, and an oven of the latter size will hold about 3000 saggers, each containing from one to a score of pieces; such an oven requires about 10–12 tons of coal in a firing of from 60 to 80 hours. The main points to be attended to are (a) firing very slowly at the commencement so as to gradually expel the water remaining in the pieces, otherwise the ware is liable to be violently ruptured; (b) gradually raising the heat and keeping it regular and equal in all parts of the oven and at no time either suddenly increasing or checking it.

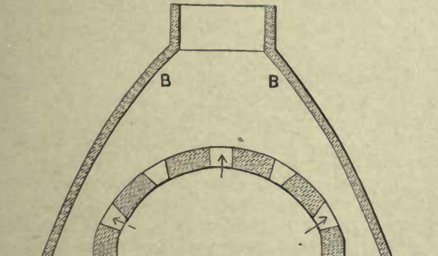


FIG. 4.—COMMON OR UP-DRAUGHT OVEN.

A. Body of oven. B. Hovel or hood. C. Mouths. D. Bag or upright chimney. D′. Other bags. *b*. Peep-hole. *e*. Bottom flues under floor of oven, running to well-hole *x*. *a*. Trial holes.

Fig. 4 represents the old or up-draught type of oven, in which the flame from the mouths, of which there are from 8 to 10 arranged at equal distances round the oven, plays directly into the firing chamber (A) by the short, upright chimneys or 'bags' (DD). Besides these chimneys, flues (ee) run from each mouth to a well-hole (x) in the centre of the oven floor; over this well-hole a bung of perforated saggers, known as the pipe-bung, is arranged, so that a portion of the flame is drawn into the centre of the oven. The ware is bedded in sand or ground flint in the saggers, which are then piled in the oven from floor to ceiling, with spaces between the piles of saggers, or bungs, to admit the free play of the flames. Holes are left at intervals round the crown to permit the escape of the fumes and the smoke. The hovel, or hood (B), is built over the whole oven to protect it from high winds and to create a good draught. The piles of saggers being arranged in rings round the central pipe-bung, and the masses of flame playing on the walls of the oven, it follows that the centre of the oven always receives less heat than the space nearer the oven walls; it is therefore necessary to arrange the pieces in the oven in such a way that the thick or heavy pieces shall get the most fire, and the flat or thin pieces least, as they are most likely to become distorted if over-fired.

The types of oven described above, though in general use in all pottery centres, are so uneconomic that numberless patents have been granted during the last 20 or 30 years for their improvement. All the ideas underlying those patents that have not seriously modified the construction may be grouped under two headings: (a) improvements in the travel of the flame and products of combustion so that more energy is utilised from the fuel burnt; (b) the conversion of the oven-mouth into a species of gas-producer so that the coal is distilled as well as burnt. In many cases the two ideas have been combined with satisfactory results. Whatever improvements have been made in this direction, and they have already been considerable, the older type of pottery kiln must remain wasteful and unscientific from the point of view of energy consumed *versus* energy produced. The ultimate solution of the potters' problem is to be sought, probably, in the following combination: (a) a relatively small kiln space maintained at a constant high temperature; (b) methods of feeding into this chamber, at correct intervals, successive batches of pottery which have been gradually heated nearly to the temperature of the firing chamber by the waste gases passing from kiln to stack; (c) removal of the ware from this chamber in such a way that it is gradually cooled, imparting its heat to the advancing air-currents, which are then economically used to consume the gaseous, liquid or solid fuel for the actual firing chamber. Alternatively, where gaseous fuel is used, the firing chambers may be built in series so as to admit of the successive introduction of (a) pottery, (b) hot waste gases for gradual heating, (c) air and gas for completion of firing, (d) air for cooling. The first method has been successfully used for years in the 'Climax' kiln for firing pottery at a comparatively low temperature as when printed, lithographed, or painted decoration has to be fired on the glazed ware; or, more perfectly, in the various types of tunnel kiln which are coming into use for the firing of pottery at higher temperatures. The second method has been adopted for kilns of the 'Glenboig' type (*v.* Eng. Pat. 3862 of 1881 and Eng. Pat. 17753 of 1890), and the 'Mendheim' and 'Siebert' kilns. (For further details, see Bourry, Traité des Industries Céramiques, 1897; Granger, La Céramique Industrielle, 1905; and Trans. Eng. Cer. Soc. vols. 2–9.)

Effects produced on pottery bodies by firing. We must briefly consider the changes produced in a body mixture by the action of fire. The most obvious effects are changes of colour, hardness and density, entire loss of plasticity, often an increased porosity, and, practically always, a shrinkage in bulk, or contraction.

Loss of water. The first effect of firing is the expulsion of all water left in the body. The body, before firing, contains water in two conditions: (*a*) the contained water that has been used to render the material sufficiently plastic for use; (*b*) the water of combination of its argillaceous constituents (*v.* art. CLAY). The contained water is readily expelled at a temperature of about 110°, but the water of combination is not expelled in all cases by exposure to a temperature of 500°, and, with very plastic mixtures only, at a full red heat. Expulsion of the contained water causes merely a shrinkage of the body and a corresponding alteration in its density, the plasticity remains undestroyed up to that point. But when the temperature has been reached at which the water of combination is expelled, the body becomes hard and brittle, loses all its plasticity, and will no longer combine with water, however finely it may be ground.

Hardness. One of the most notable qualities of natural clays is their property of becoming hard and durable when raised to a red heat; but in the case of pottery bodies containing other materials besides plastic ones, the degree of hardness is necessarily different from that of a natural clay heated to the same temperature. The more fusible matter the body contains, the greater is its hardness at all temperatures above that at which fusion begins, whilst bodies containing a large excess of free silica, or an excess of lime, can generally be scratched by a good knife, even after a severe fire. As a general rule, the hardness of a fired body agrees with its density, whilst it almost invariably increases with an increased temperature of firing. The following rough classification shows how the different pottery bodies stand in this respect:—

1. Scratched with a knife, readily: almost all ancient pottery and majolica (body).
2. Scratched with a knife, but with difficulty: bodies of the first class of modern manufacture.
3. Not touched with a knife, but abraded by a good file: well fired earthenware (biscuit).
4. Not scratched by a steel tool: bodies of the third class and many stoneware and mortar bodies.

Density. The variations in density which pottery undergoes in firing are by no means well understood. With ordinary bodies there is generally an increase of density, varying with the degree of fire; but with some of the bodies of the third class the increase in density appears to be very irregular. Thus with English bone porcelain, and, according to Brongniart, in the case of hard porcelain too, although there is a considerable shrinkage of the body in firing, yet not only does the body lose weight in the firing, but it loses it at such a rate as to outstrip the loss of size so that the density of the fired body is less than that of the unfired body. English bone china, again, when overfired, suffers a great diminution in density consequent upon a sudden expansion of the article.

Shrinkage. The contraction which all bodies undergo on firing depends upon three things: (*a*) the nature of the mixture; (*b*) the method of fabrication; (*c*) the firing conditions. Contraction due to the nature of the body either results from the expulsion of the contained water, which may cause a contraction of from 10 to 15 p.c. in those containing a very large proportion of plastic ingredients, or from the partial vitrification of the body, *e.g.* 'parian,' which contains a large proportion of felspar, contracts as much as 20 p.c. from the 'dry' to the 'fired' size. The influence of different proportions of plastic, aplastic and fusible materials in the body is well shown in the three following mixtures:—

No. 1.

Ball clay	10 p.c.
China stone	7 ,,
Flint	80 ,,
Lime	3 ,,

No. 2.

Ball clay	25 p.c.
China clay	10 ,,
China stone	60 ,,
Flint	5 ,,

No. 3.

Ball clay	60 p.c.
China clay	20 ,,
China stone	10 ,,
Flint	10 ,,

These bodies were fired at 1150°, being placed in the same sagger, in the form of dry tiles pressed from dust. No. 1 exhibited no contraction, No. 2 ran in 25 p.c., and No. 3 ran in 20 p.c.

The contraction due to the loss of water connotes only physical changes, but that due to the partial vitrification of the body materials generally denotes more profound rearrangement of the ultimate molecular structure. The effect of both these changes is strongly marked in the case of hard porcelain, which when submitted to the first or hardening fire, *feu dégourdi*, shrinks about 3 p.c. from loss of water, which is entirely expelled by this firing; but when this dehydrated ware is afterwards raised to incandescence a further contraction, amounting to nearly 7 p.c., takes place because of the interactions between the various constituents of the body.

The methods by which any given article has been shaped also modifies the amount of contraction; the ware subjected to the greatest pressure in making will contract least in firing with any given body. Moulded or pressed ware contracts less than thrown ware, and this considerably less than cast ware, although all may be made from the same mixture and fired to the same temperature.

Colour. For the effect of fire on the colour of ordinary ferruginous clays, *v.* art. CLAY, and also Appendix A, p. 276, of Catalogue of Pottery in Jermyn Street Museum. As almost all varieties of plastic clay contain sufficient traces of iron compounds to produce at least a pale cream or ivory-coloured body when fired, it is customary, in the manufacture of very white earthenware, to add a small quantity of cobalt oxide, which by the production of a blue silicate of cobalt neutralises the effect of the yellow tone due to the iron compounds; 1 part of cobalt oxide is sufficient to whiten about 2000 parts of cream-coloured body. Excess of flint or china clay and addition of lime or magnesia to the clay also whiten the fired body to a marked degree. The colour of a fired body is also influenced by the nature of the kiln atmosphere during the last stages of the firing. The whiteness of hard porcelain, although the mixture contains traces of oxide of iron, is due to the fact that the firing is finished in a reducing atmosphere. On the other hand, bricks that would burn to a deep red colour in an ordinary oxidising fire are converted into 'blue' bricks by finishing the firing in an atmosphere charged with smoke. For specially coloured bodies, *see* section on *Colours* in this article. The following table gives the percentage composition of some of the more important pottery bodies after firing :—

——	Silica	Alumina	Lime	Magnesia	Potash	Oxide of iron	Bone earth	Analyst
Sèvres hard porcelain 1770–1830	58·00	34·50	4·50	—	3·00	—	—	Malaguti
Vienna (imperial) hard porcelain, 1806	61·50	31·60	1·80	1·40	2·20	0·80	—	Laurent
Berlin hard porcelain, 1808	66·60	28·00	0·30	0·60	3·40	0·70	—	„
Meissen hard porcelain (*dégourdi*), 1825	57·70	36·00	0·30	—	5·20	0·80	—	„
Meissen hard porcelain (baked) 1825	59·40	32·60	—	—	5·50	0·40	—	„
Chinese hard porcelain	70·50	20·70	0·50	0·10	6·00	0·80	—	Malaguti and Laurent
Bristol hard porcelain, 1775–1780	62·92	33·16	1·28	—	2·64	—	—	Church.
English chinaware, 1847	39·88	21·48	10·06	—	2·14	—	26·44	Cowper
English chinaware, 1889	41·01	23·05	—	—	2·46	0·10	33·09	Author.
English earthenware (cream colour), 1889	63·10	33·09	1·05	0·12	0·22	2·10	—	„
English earthenware (granite) 1889	70·90	27·25	1·00	—	0·10	1·02	—	„
English stoneware (Lambeth)	74·00	22·04	0·60	0·17	1·06	2·00	—	Salvétat
English stoneware (Wedgwood)	66·49	26·00	2·04	0·15	0·20	6·12(?)	—	„
English red facing brick of good quality	51·01	36·90	0·24	2·01	—	9·98	—	Author
English firebrick of good quality	70·86	24·68	0·21	0·63	—	2·90	—	„
Saggers used in Staffordshire	68·24	26·31	0·18	—	—	4·89	—	„

Glazes and glazing. In discussing the various pottery bodies, it has been pointed out that some of them contain a sufficient proportion of fusible material (natural or artificial) to approach vitrification at the temperature used for manufacture. Such bodies become sufficiently impervious to fluids to serve many useful purposes, but, in the majority of cases, the body remains porous after firing and, for use or beauty, must be coated with a definite vitreous envelope or surface-layer known as the glaze.

All glazes are found to contain silica, alumina and one or more of the alkaline or alkaline-earth bases as necessary ingredients. For centuries the majority of glazes have contained lead oxide in addition, and, for the last 150 years or so, many glazes have contained boric acid as well. Chemically a glaze is a rapidly solidified solution in which silica, silicates, borates, &c., may either be solvents or solutes. For colouring or opacifying purposes metallic oxides, phosphates, &c., may be dissolved or suspended in them. If we regard a vase or a plate only, it is natural to think of the glaze as a distinct layer of glassy material melted over the surface of the pottery, but in no case is this simple view sufficient; in every case the glaze and body react with each other on fusion, and there is always an intermediate layer of glaze-body or body-glaze, while in such instances as salt-glaze, or the common lead glazes obtained by melting lead oxide on the ware itself, the greater part of the silica and alumina needed to form the glaze are obtained from the surface of the ware by the action of soda or lead oxide at a high temperature. Between such simple types of glaze and those hard porcelain glazes which consist practically of fused felspathic rock we find every grade of chemical and physical complexity.

A perfect glaze would possess the following properties :—

1. It should be clear, brilliant, and thin, so as not to hide modelled work.
2. It should have such a suitability to and agreement with the body, as neither to chip off from the sharp edges of the body nor to break up into minute cracks (crazes) upon the surface.
3. It should be hard enough to resist wear, especially if used for culinary purposes.
4. It should not be attacked by water nor by acid vapours, and if used for culinary, domestic, or sanitary purposes should not be attacked by any ordinary dilute acid.
5. It must bear exposure to the conditions of firing and cooling, whether rapid or prolonged, without devitrification.
6. For the majority of purposes it must be so

tenacious as not to run off upright objects when melted, but it must flow smoothly and evenly on flat surfaces.

7. When a glaze has to be used over printed or painted decoration, it must not have too great a solvent action on the substances used for these purposes.

8. When a glaze is to be coloured, its nature must be such that it can contain metallic compounds in solution or suspension without unsightly separations.

No glaze answers to all these requirements, but centuries of practical experience have established certain types which may be accepted as the best for their special purposes. Many ancient glazes possess certain æsthetic qualities of rare charm, but the glazes devised during the last two centuries mark a great advance in technical accomplishment. Before proceeding to the question of glazes in general, a brief account of salt-glazing is desirable.

Salt-glazing.—For the salt-glaze process only such bodies can be used as contain a considerable excess of silica uncombined with alumina. When ware of this nature is fired in a kiln with free circulation of the flame and smoke amongst it, the most expeditious method of producing the glaze is to throw on to the fires at the termination of the firing a quantity of wet salt, or it may be thrown directly into the oven. Vapours of common salt and water thus pass into the oven and a mutual decomposition takes place between them, resulting in the formation of hydrochloric acid vapours and the liberation of soda, which immediately combines with the silica and alumina of the ware, with the formation of a coating of a hard insoluble glass upon the surface exposed to the action of the fumes. It has been found in practice that clays with a wide range of composition can be successfully glazed in this way, say, where the ratio $Al_2O_3 : SiO_2$ varies from $1 : 4{\cdot}6$ to $1 : 12{\cdot}5$; but in general this ratio is about $1 : 8$ (*v.* Trans. Amer. Ceramic Soc., 4, 211). Salt-glaze is therefore a soda-alumina-iron-silica mixture of variable composition.

Another simple type of glaze, analogous to the foregoing, is that used on the common red and brown wares of many countries, obtained by coating the unfired clay vessel with powdered galena, red lead, or litharge. In this case the molten lead oxide attacks the surface of the article and produces a rich and brilliant glaze consisting of a lead-alumina-iron-silica mixture, often containing much uncombined lead oxide.

The most important glazes are those used on the earthenwares and porcelains, for these exhibit the greatest diversity of composition and are in general use in most civilised countries. They range from the hardest porcelain glazes, consisting of little but felspar and quartz, to the softest earthenware glazes which contain silica and boric acid, together with alumina, lead oxide, lime, soda, and other bases. It is convenient to express the composition of glazes in a conventional manner so as to exhibit the ratio which the components bear to each other. This is usually done by treating the sum of the monoxide bases (reckoned molecularly) as unity and calculating the sesquioxides and dioxides proportionately. The general formula thus becomes $1RO : xR_2O_3 : yRO_2$, and it is found that x is generally less whilst y must always be greater than unity. The RO constituents may be the oxides of lead, zinc, calcium, barium, potassium, sodium, &c.; the R_2O_3 constituent is generally alumina or alumina and sesquioxide of iron, and the principal RO_2 constituent is silica, which may in part be replaced by boric or titanic acid, &c.

It has been found that all practicable glazes lie between $1RO : 0{\cdot}1R_2O_3 : 1{\cdot}5RO_2$ and $1RO : 1{\cdot}25R_2O_3 : 12RO_2$.

It follows, from the general laws governing the fusibility of mixtures, that the more bases there are in the RO group, the lower will be the melting-point of the glaze, whilst it is equally apparent that the replacement of some of the silica by boric acid will tend in the same direction. The part played by alumina, the principal member of the R_2O_3 group, is of the utmost importance, for no stable glaze can be obtained without it, and the ratio it bears to the other constituents influences the working properties of the glaze, and especially its viscosity when melted. The hard porcelain glazes are rich in alumina and silica and comparatively poor in the members of the RO group, as we should expect from the fact that they are generally prepared from mixtures of felspar and quartz, occasionally with a little calcium carbonate. Practicable glazes of this type fall within the following limits—$1RO : 0{\cdot}2R_2O_3 : 3{\cdot}5RO_2$ and $1RO : 1{\cdot}25R_2O_3 : 12RO_2$, the first representing the ordinary glazes of Chinese porcelains and the last that of the most refractory European porcelains. It must also be borne in mind that in these glazes the RO group contains only soda, potash, lime, or magnesia. The glazes of earthenware and English china are widely different both in type and constitution. They include mixtures of every degree of fusibility, between 1000° and 1150°; they have less analogy with the body than the porcelain glazes and they are applied to 'biscuit' ware which has already been fired to a higher temperature, so that there is not the same intimate relation between glaze and body. For convenience of description, we may divide them into two groups: (*a*) raw glazes; (*b*) fritted glazes. In the first group, as all the ingredients are insoluble in water, it is sufficient to grind them together before applying the mixture to the body; in the latter, the soluble ingredients (soda, borax, &c.) must be melted with a portion of the silica, lime, or clay into a fritt or glass so as to render them insoluble in water. This fritt is then weighed out, together with the requisite proportions of flint, china stone, white lead and such other insoluble materials as are necessary, and the mixture is ground together on a pan similar to the one shown in Fig. 1, or in a grinding cylinder, until it is perfectly fine. The glaze, in suspension in water, is then put into convenient receptacles and the biscuit-ware dipped in it—a portion of the water is absorbed, and a thin coating of powdery glaze is left on the piece. The articles are placed in saggers, being carefully supported on pointed supports; the saggers are piled in bungs in ovens such as those shown in Fig. 3 or 4, and the whole is submitted to a second firing, less in intensity than the first or 'biscuit' firing, but sufficient to melt the glaze over the surface of the ware. The older form of oven shown in Fig. 4 answers better for glazing than the down-draught form shown in Fig. 3, because in the latter form the fumes and products of combustion, being kept longer in the oven, are more likely to penetrate the saggers and damage the brilliance of the glaze. It is advisable to lute the saggers together with a roll or 'wad' of clay for the 'glost' fire, so as to check the penetration of fumes into the saggers during firing. With the more fusible kinds of glaze, such as are used for the decoration of English majolica, the pieces, after dipping, instead of being enclosed in saggers, are often placed in a kiln or large muffle similar to the one shown in section in Fig. 5. This kiln takes the place of one big sagger, and the flame playing all round it raises the kiln and all its contents to a temperature sufficient for the fusion of glazes rich in lead, such as are used for these purposes. Glazes of this type approach the formula—

$$1RO : 0{\cdot}3R_2O_3 : 3{\cdot}5RO_2,$$

but the RO group may contain oxides of sodium, potassium, calcium, barium, zinc, or lead, and in the RO_2 group, boric acid always replaces a portion of the silica.

Glazes that when fired may appear very similar, to any one who is not expert, may be as different as—

$$\left.\begin{array}{l}0{\cdot}40\ PbO\\0{\cdot}38\ CaO\\0{\cdot}06\ K_2O\\0{\cdot}16\ Na_2O\end{array}\right|0{\cdot}25\ Al_2O_3\left\{\begin{array}{l}2{\cdot}75\ SiO_2\\0{\cdot}59\ B_2O_3\end{array}\right.$$

and

$$\left.\begin{array}{l}0{\cdot}3\ K_2O\\0{\cdot}2\ Na_2O\\0{\cdot}3\ CaO\\0{\cdot}2\ BaO\end{array}\right|0{\cdot}1\ Al_2O_3\left\{\begin{array}{l}3{\cdot}4\ SiO_2\\0{\cdot}6\ B_2O_3\end{array}\right.$$

with corresponding differences of melting-point, fluidity, &c. The glazes rich in lead are more fusible and generally simpler in use than those in which the RO group comprises only alkaline and alkaline-earth bases. The concentration of pottery manufacture in certain districts in each country has brought about a specialisation of the industry such as did not exist when pottery was only a handicraft. This change has caused certain evil effects of the potter's calling to need redress from statesmen and philanthropists. Lead glazes may be harmless to the worker or the user, but where occupation or use is constant, with certain glazes, some risk of plumbism follows. It is important to distinguish between the lead poisoning of the operative, caused by the use of lead compounds in glazes, and that due to lead oxide dissolved from a fired glaze by the acids used in cooking which falls on the user of the article. This latter and minor evil has not arisen in England, but in Germany an Imperial Edict has been enacted (Ref. Thorpe and Oliver, Cd. 9207 of 1899), specifying that glazes are not to be applied to articles intended for culinary use unless they will resist, when fired, the solvent action of strong, boiling acetic acid. Plumbism arising among the operatives who handle lead compounds in various manufacturing processes has given rise to many investigations in England (Thorpe and Oliver, Report to the Home Secretary on the use of Lead Compounds in Pottery, Cd. 9207 of 1899; Burton, W., The Hygiene of the Pottery Trade, Shaw Lecture, Royal Society of Arts, Feb. 1908; Report of Departmental Committee, Home Office, 1908–1910, Cd. 5219, 5278, and 5385 of 1910).

The following table gives the composition of a few typical lead glazes, from the harder ones used for bone china to the softer ones used for English majolica ware :—

—	Fritt							Glaze			
	Borax	Chalk	Flint	China stone	Felspar	Soda	Kaolin	Fritt	Flint	China stone	White lead
English—											
China glaze .	50	16	40	24	33	—	—	45	—	15	15
Earthenware glaze	48	38	62	—	—	26	30	230	60	160	120
Granite glaze .	80	30	80	100	40	40	30	360	50	50	80
Majolica glaze .	40	20	40	100	—	12	—	100	—	10	120
Parian glaze .	20	—	15	20	—	—	5	20	—	—	64
Soft tile glaze .	—	—	—	—	—	—	—	—	11	22	56

These recipes might be multiplied a hundredfold, but sufficient are here given to show the general lines of their composition, and they represent glazes in actual use.

Coloured glazes.—During the last century or so a great variety of coloured glazes have been introduced, especially for the decoration of wall tiles. The foundation of these glazes is in most cases a fritt rich in lead; and for the turquoise blues derived from cupric oxide, a fritt with a base of silicate of soda and lime. In every case the object is to get a glaze presenting a rich luscious appearance and fusible at such a low heat as not to impair by volatilization or otherwise the tone of colour produced by the addition of small quantities of oxide of copper, oxide of manganese, oxide of iron, &c. The following mixture was given by Salvétat in the Dictionnaire des Arts et Manuf., as suitable for the production of a variety of coloured glazes adapted to soft porcelain, earthenware, or tile bodies :—

Red lead . . .	2000	grms.
Flint	1000	„
Calcium borate . .	500	„

This forms a colourless fusible glaze, and by the addition of the various colouring oxides any desired variety of shade can be produced. Blues by the addition of from 40 to 125 grms. of cobalt oxide to the above quantity of glaze; blue-greens by the addition of from 100 to 500 grms. of cupric oxide to the above quantity of glaze; ivory to strong yellow by the addition of from 70 to 200 grms. of ferric oxide to the above quantity of glaze; madder-brown to purple-brown by the addition of from 70 to 125 grms. of manganic oxide to the above quantity of glaze, and various intermediate tints by admixture of the different oxides in various proportions. The mixture of glaze materials and colouring oxide is ground coarsely together, melted in crucibles, poured out into water and ground fine; in this way a more perfect combination is obtained than by simply grinding the materials together. An English mixture serving the same purposes, but not quite so fusible nor so generally applicable to the various bodies as the one given above, is made by grinding together flint 100 parts, china stone 90 parts, red lead 360 parts, borax 40 parts. The mixture is fritted in flinted saggers, ground and then various proportions of finely-ground metallic oxides are added to it for colouring purposes. These glazes may be applied by dipping like ordinary glazes but they are often applied by large camel-hair pencils or blown on by compressed air, and mingled tints produced in this way are often exceedingly beautiful.

The question of the composition and constitution of all the various types of coloured glazes is too complex to be treated here; for details the reader must refer to the more important treatises given in the bibliography at the end of the article and to the proceedings of the ceramic societies of this and other countries.

The stanniferous glazes, or enamels, as they are more generally called, are not so largely used now, except for the manufacture of white glazed bricks, as they were at the time of the Renaissance and later, when the famous Italian Majolica and Della Robbia wares and the Delft of Holland were decorated on a ground of opaque tin enamel. A revival of this manufacture has, however, taken place during the last sixty or seventy years; and in Italy, France, Germany, and Holland many factories still manufacture faïence with a stanniferous glaze. The following recipes are given by Deck for the principal enamels of this class:—

White.—Lead and tin ashes, 44; sand, 44; soda, 2; common salt, 8; red lead, 2.

Yellow.—White as above, 91; antimony oxide, 9.

Blue.—White as above, 95; cobalt oxide, 5.

Green.—White as above, 95; cupric oxide, 5.

Yellow-green.—White, as above, 94; cupric oxide, 4; lead antimoniate, 2.

Violet.—White, as above, 96; manganese dioxide, 4; although of course the exact composition of the glaze will depend upon the body to which it is to be applied.

Bodies very rich in fusible materials like parian and some of the finer stonewares, become quite impervious to liquids and acquire a smooth and glossy surface without the application of a glaze, from the semi-vitrification of the body itself. Opener and less fusible bodies than these acquire a similar surface if they are fired in saggers, the insides of which have been washed with glaze rich in oxide of lead and containing chlorides or fluorides. Mixtures of oxide of lead with cryolite, fluorspar, common salt, calcium chloride, &c., are the best for this purpose. When heated, they probably give off volatile fluorides or chlorides of lead and these are again decomposed on the surface of the ware forming a thin smear or coating of lead silicate. One of the common defects of glazes—the separation of certain compounds on cooling—has, in recent years, been cultivated so as to produce effects of rare beauty. Glazes rich in zinc oxide are apt to develop crystals of willemite (zinc silicate) on cooling, and at Copenhagen, Sèvres, and Berlin the preparation of such glazes has been raised almost to a fine art. Other glazes yield beautiful small crystals of various micas and of this kind the 'Aventurine' glazes of Pilkington's, introduced by Joseph Burton, are highly esteemed (*see* Burton, W., Crystalline Glazes as Pottery Decoration, Journal Soc. of Arts. 1902).

Colours. No department of pottery has made such advances during this century as the preparation of the various ceramic colours, and while at the beginning of the last century the colours were, for the most part, fired *on* the glaze at low temperatures, we now possess coloured bodies, under-glaze colours, and on-glaze colours in abundance. Owing to the fact that all pottery colours require to be submitted to at least a red heat, no organic colours can be used for this purpose, and recourse must therefore be had to such inorganic compounds as will produce colour effects without decomposition at high temperatures and under the solvent action of glazes and fluxes. The list of substances which answer these requirements is by no means a large one, comprising only the oxides of cobalt, nickel, iron, manganese, zinc, copper, antimony, lead, uranium, and iridium, a few salts, such as chromates of iron, lead, and barium, the natural ochres, purple of Cassius, and a few obscure compounds such as chrome-tin pink. For the preparation and properties of each of these substances reference must be made to the respective articles in this work, in which they are treated at length.

Coloured bodies. In almost every form of pottery belonging to classes 2 and 3, it is possible to stain the white bodies with various colours; but owing to the fact that they have to endure the most intense heat used by the potter, the number of colours is very limited. The bodies rich in fusible materials, especially those rich in felspar, stain most beautifully, as the felspar forms a neutral flux in which the particles of colouring matter are dissolved and so produce their richest effects. Mosaic tiles and tesseræ, coloured parians, porcelains, and jaspers are the best examples of coloured bodies. They are all rich in fusible materials. The following are a few of the proportions used:—

Blue (pale), 95 parts of body; 5 parts of cobalt oxide.

Blue (strong), 90 parts of body and 10 parts of cobalt oxide.

Green, 85 parts of body, 5 parts of cobalt oxide; 10 parts of chromium oxide.

Blue-green, 95 parts of body; 2½ parts of chromium oxide; 1¼ parts of cobalt oxide; 1¼ parts of zinc oxide.

Bronze-green, 95 parts of body; 5 parts of calcined nickel oxide.

Brown, 85 parts of body; 15 parts of calcined iron oxide.

Yellow, 90 parts of body; 10 parts of titanium oxide.

Black, 90 parts of body; 7 parts of iron oxide; 3 parts of cobalt oxide.

In the style of decoration known as 'barbotine' or slip painting, colouring oxides are often added to the ordinary earthenware or stoneware mixtures, but the effect is much inferior in juicy richness unless the article be afterwards glazed.

Under-glaze colours. These colours, consisting for the most part of oxides, chromates, or silicates, mixed with china clay, flint, &c., so as to diminish the action of the glaze upon them, or to assist in the development of the tone of colour required, are applied on the biscuit-ware before the piece is glazed. They must therefore resist the action of the glaze at a temperature sufficient to melt the latter; they must be infusible enough to remain *still* under it; and they must have such an agreement with both the glaze and the body as not to cause the glaze to fly off in flakes. The following colours answer well for both china and earthenware:—

Black, 8 parts of native iron chromate; 3 parts of Mn_3O_4; 3 parts of CoO; 1 part of flint, calcined together strongly and then ground fine.

Dark blue, 4 parts of CoO; 1 part of flint; 1 part of chalk, ground together.

Azure blue, 60 parts of ammonium alum; 3 parts of cobalt oxide; calcined strongly, then ground and washed thoroughly until free from traces of acid.

Blue-green, 12 parts of borax; 12 parts of chalk; 12 parts of zinc oxide; 24 parts of green oxide of chromium; 4 parts of cobalt oxide; calcine well together and grind until fine.

Dark brown, 8 parts of native iron chromate; 4 parts of zinc oxide; 2 parts of iron oxide ground well together, calcined strongly and reground.

Red-brown, 6 parts of precipitated iron chromate; 20 parts of zinc oxide; 3 parts of litharge; calcine together strongly and then grind fine.

Pink colour: tin oxide, 100; chalk, 34; chromium oxide (Cr_2O_3), 1; silica, 5; mixed well together, calcined strongly, and ground.

Yellow: antimony oxide, 3; red lead, 6; flint, 2; tin oxide, 1; calcined together and then ground.

In all these colours the important point is to have the materials well ground together before calcining to promote their union and the value of the tint is much improved if the final grinding be as complete as possible.

On-glaze colours. These colours are really fusible glasses, of such a nature that when they are applied upon the fired glaze and the article is refired at 700°–800°, they become fused to its surface. Unless this union with the glaze be perfect, such colours are always liable to wear off, and they never have the richness of under-glaze colours owing to the lower temperature at which they are fired. On-glaze colours are divided into the two classes of regular-kiln colours and hard-kiln colours, the latter colours containing a smaller proportion of flux than the former and hence requiring a higher temperature of firing.

The first requisite in on-glaze colours is a series of fluxes which shall accord well with the glaze, shall fuse at a sufficiently low temperature, and shall fuse the particles of colouring matter without decomposition. Salvétat prepared a series of fluxes which answer perfectly for hard porcelain. Their composition is as follows:—

—	No. 1 Flux	No. 2 Flux	No. 3 Flux	No. 4 Flux	No. 5 Flux
Litharge	75·0	66·66	11·12	37·50	73·00
Silica	25·0	22·22	33·33	12·50	9·00
Calcined borax	—	11·11	55·55	—	—
Boric acid	—	—	—	50·00	18·00

No. 1 is a special flux for certain dark-blues fired in the hard kiln; No. 2 is the general flux for browns, greys, yellows, and iron-reds; No. 3 is the flux for carmines made from gold, and No. 4 for gold purples; No. 5 is the peculiar compound used for greens prepared from chromium oxide—a flux used for a similar purpose at Meissen was composed of 73 parts of litharge, 18 parts of silica, and 9 parts of boric acid.

The fluxes used in England differ considerably from the foregoing on account of the different types of glaze to which they are applied; in this country almost every colour-maker has fluxes of his own, and there is considerable difficulty in arriving at anything like a general statement as to the composition of the fluxes used. The following compositions are for fluxes largely used in Staffordshire:—

—	No. 1 Flux	No. 2 Flux	No. 3 Flux	No. 4 Flux	No. 5 Flux
Red lead	64·50	49·99	30·55	15·76	40·00
Silica	21·50	16·66	41·68	21·19	20·00
Borax (cryst.)	—	33·33	27·77	63·05	40·00
Flint glass	14·00	—	—	—	—

No. 1 is a special flux for a brilliant scarlet preparation from lead dichromate; and the remainder are used for the same purposes as the similarly numbered French fluxes described before.

The preparation of all the fluxes is as follows: The various ingredients are ground together dry and then melted in good crucibles; when melted they are poured out either into water or on a slab, the latter method being preferable, as fluxes rich in borax are readily attacked by water. They are then ground to a fine powder and are ready for mixing with the colouring agent.

The following typical mixtures will serve as an indication of the general composition of on-glaze colours; the proportions of colour and flux remain good in all cases, the only point being to use a suitable flux:—

Regular-kiln colours:—

Strong grey.—Flux No. 2, 68 parts; cobalt carbonate, 6; ferric hydrate, 13; zinc carbonate, 13.

Pale grey.—Flux No. 2, 92 parts; cobalt carbonate, 5; ferric hydroxide, 3.

Strong black.—Flux No. 2, 80 parts; cobalt carbonate, 10; ferric hydroxide, 10.

Iridium black.—Flux No. 2, 75 parts; iridium sesquioxide, 25.

Uranium black.—Flux No. 2, 75 parts; black oxide of uranium, 25.

Strong blue.—Flux No. 2, 61 parts; cobalt carbonate, 13; zinc carbonate, 26.

Pale blue.—Flux No. 2, 80 parts; cobalt carbonate, 6; zinc oxide, 14.

Blue-green.—Flux No. 5, 75 parts; cobalt carbonate, 6; green oxide of chromium, 19.

Sea-green.—Flux No. 2, 80 parts; copper carbonate, 20.

Pale-yellow.—Flux No. 1, 80 parts; potassium antimoniate, 14; zinc carbonate, 6.

Orange.—Flux No. 1, 80 parts; potassium antimoniate, 14; red oxide of iron, 6.

Uranium orange.—Flux No. 1, 75 parts; yellow oxide of uranium, 25.

Yellow-brown.—Flux No. 2, 75 parts; ferric oxide, 10; zinc carbonate, 15.

Red.—Flux No. 2, 75 parts; red ferric oxide, 25.

Rose colour.—Flux No. 3, 87 parts; purple of Cassius, 12; precipitated silver, 1.

Purple.—Flux No. 4, 90 parts; purple of Cassius, 7; gold oxide, 3.

All these colours, with the exception of the last three, are made by grinding together the constituents, then fusing the mixture in crucibles, and regrinding perfectly fine. Of the remaining three colours, the red from oxide of iron needs most careful preparation. The oxide for this purpose is prepared by carefully calcining dried ferrous sulphate until the brilliant red tint is fully developed, which takes place between 400°–420°. Below this temperature a dirty yellowish brown, and above it a purplish-brown product, is obtained. The oxide of iron and flux are simply ground together, not calcined.

The colours obtained from gold are obtained by mixing the ingredients well together, and submitting the mass to a gentle calcining at a temperature below redness; they vary in tint with the degree of heat to which they are subjected, changing from a full rose-colour at a clear red heat to a dullish purple at a heat approaching whiteness.

Hard-kiln colours.

These colours are prepared from materials similar to those used for regular-kiln colours, but they contain a smaller proportion of flux. Owing to the greater heat to which they are subjected, the number of compounds which can be used is more limited than in the former case; but the colours become so fused into the glaze that they attain an added richness and brilliancy, and at the same time gold and other metals can be applied over them for decorative purposes.

Metals.—Only the noble metals can be applied in the metallic state for the decoration of pottery, and of these only gold, silver and platinum are in actual use. The preparation of the gold for pottery purposes necessitates its production in as fine a state of subdivision as possible. Three methods are in use for this purpose:—

1. The French method, in which the gold is obtained in a finely divided state by precipitating a very dilute solution of the chloride with a dilute solution of ferrous sulphate (*v.* art. GOLD). The precipitated gold, after careful and repeated washings, is dried and ground with $\frac{1}{12}$th of its weight of bismuth nitrate or of calcined borax; this powder is then made up into a pigment by mixing it with oil of lavender or fat turpentine, and when fired the bismuth salt or the borax serves to flux it to the glaze.

2. The English method, by which an amalgam of equal parts of gold and mercury is prepared, mixed with $\frac{1}{10}$th–$\frac{1}{12}$th of its weight of the No. 2 flux given above, and ground under water to an impalpable powder. This is dried, mixed with fat oils, and applied, like the other, and when fired the mercury volatilises, leaving the gold with a dead or matt surface, which is then brightened by scouring with sand and burnishing with agate, bloodstone, &c. Silver and platinum are seldom used by themselves but, by adding from 12 p.c. to 25 p.c. of them to pure gold, light and green golds are produced which are much prized as additional decorative resources in rich gilding.

For very elaborate and expensive work, gold is sometimes prepared by grinding gold-leaf under water with the requisite amount of flux. The powder thus obtained is dried, and ground up with honey to a workable consistency. It is applied thickly, and after firing can be chased and cut up with agate chasers. This was the method of gilding used on the finest examples of the soft porcelain of Sèvres.

3. What is known as 'liquid' gold is now in common use. A fluid mixture is prepared by pouring a solution of auric chloride into an oily menstruum. This may be painted, printed, or otherwise transferred to the glazed surface, and on firing a brilliant deposit of gold is left which does not need burnishing. This method is analogous to that by which the gold and silver lustres of the eighteenth and nineteenth centuries used on common pottery were obtained, the so-called 'silver' lustre being a film of platinum (*v.* below).

Lustres. Iridescent metallic films have been used as a means of pottery decoration since the ninth century, and the lustred wares of the Persian, Italian, and Hispano-Moresque potters (ninth to sixteenth centuries) have formed the subject of many treatises. After centuries of neglect this elegant process has been revived during the last fifty years, and, in many countries, it is again used as a distinctive pottery decoration. In principle it consists in the production of films of silver or copper on a fired glaze, but the films are of such exquisite tenuity that they glow with interference colours like a soap bubble, as well as with the yellow colour which silver, or the red colour which copper, imparts to a glaze. The term 'lustre' has been carelessly applied to pottery covered with thin metallic films of gold or platinum (eighteenth century and later). In speaking of lustre, the term ought to be restricted to those metallic films that are so thin as to be iridescent (*v.* Burton, W., Lustre Pottery, Journ. Roy. Soc. of Arts, 1907, vol. 55). The term 'lustre' is also commonly used for certain compounds with a bismuth salt as base, which when fired in an ordinary kiln leave pearly films, which are feebly iridescent, but these are fired at so low a temperature that they are not very durable and they always lack the artistic charm of true lustre decoration.

Application of colours. The colours are applied by painting, stencilling, the transfer of printed or lithographed patterns, and in a variety of minor ways. In each case the colour is mixed with a resinous medium to give it body. For printing purposes it is made into a kind of ink or pigment by mixing with thick, boiled linseed oil. The mixture is then worked into an engraving or etching on a flat copper plate or roller; the excess of colour is removed, and a print taken from the engraving on thin tissue-paper. Lithographs are prepared much in the usual way. The paper print or lithograph is then applied to the required article; in the case of under-glaze colours on the biscuit ware, and in the case of on-glaze colours on the glazed ware. The porous biscuit ware readily absorbs the colour from the paper when rubbed, and the paper can then be washed or pulled off. Glazed pieces are first 'primed' with a size made by thinning Canada balsam with turpentine; this size serves to absorb the colour, and after standing some time the paper is washed off, leaving behind a perfect impression in colour. The ware then requires to be fired, and this firing is effected in a closed kiln or muffle, shown in section in Fig. 5. The ware is skilfully piled in this; in the case of biscuit ware it is heated to full redness to expel the printing oils, and leave the ware in a condition to receive the glaze; in the case of on-glaze colours, the firing is carefully regulated to suit the particular colours in question. During recent years much printed biscuit ware is no longer heated to drive out the oil, but the latter is sufficiently saponified by washing the piece in a bath of dilute acid, so that a sufficient coat of glaze adheres when the pieces are dipped.

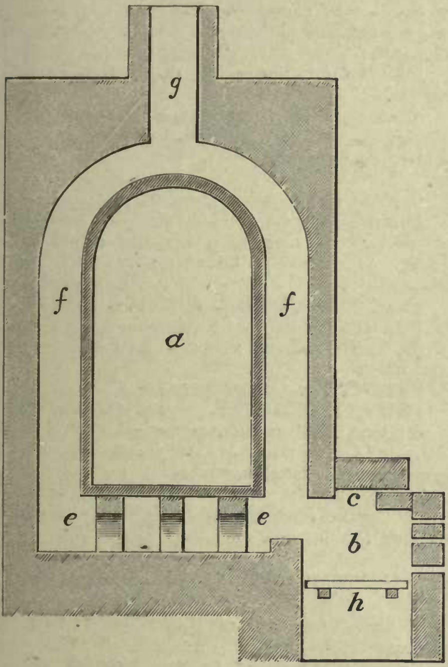


FIG. 5.—TRANSVERSE SECTION OF ENAMELLING KILN.

a. Kiln. *b*. Fireplace, charged at *c*. *e*. Bottom flue. *f*. Upright flues. *g*. Chimney.

In painting, the colours, whether under-glaze or on-glaze, are mixed up into workable pigments with fat, turpentine, oil of lavender, aniseed, &c., and applied with camel-hair pencils in the ordinary way.

Metals are usually fluxed, so as to adhere perfectly to the glaze at the heat necessary to fire the on-glaze colours.

Various pyrometers and pyroscopes have been devised for pottery purposes from the 'contraction' pyrometer of Wedgwood to the fusible cones of Seger (*v.* art. PYROMETRY; also Burton, W., Trans. Eng. Ceramic Soc. vol. 6; and Darling, Industrial Pyrometry (Cantor Lectures, Roy. Soc. Arts. 1910–1911)); but in practical work the fireman usually judges the progress of the firing by small trials of a similar substance to the material being fired, which he removes from the kiln from time to time as the firing progresses.

Literature. Brongniart's great work, Traités des Arts Céramiques, especially the edition of 1877, with additions by Salvétat, laid the foundation of modern ideas, but is now out of date. Salvétat published many valuable essays, notably his Leçons de Céramiques. Seger's collected writings (German edition, 1895; English translation, 1902) mark an epoch because they furnished a fresh starting-point for later investigators in all countries. The Sprechsaal in Germany; the Comptes Rendus, and other publications of the Academy in France; Transactions of the English Ceramic Society and those of the American Ceramic Society, record current progress. A few works such as Langenbeck, Chemistry of Pottery, 1895; Auscher, Technologie de la Céramique, 1901; Bourry, Traité des Industries Céramiques, 1897, English translation, 1901; Schamberger, Die Keramische Praxis, 1901; Granger, La Céramique Industrielle, 1905; B. Kerl, Handbuch der Gesammten Thonwaarenindustrie, E. Cramer and H. Hecht's edition, 1907; and K. Dümmler, Handbuch der Ziegel Fabrikation—new edition to be published in eighteen parts of which twelve parts have appeared—are convenient text-books of modern theory and practice.

W. B.

POUDRE B *v.* EXPLOSIVES.

POZZUOLANA *v.* CEMENT.

PRASEODYMIUM. Sym. Pr.; at.w. 140·6. One of the two metallic components of the rare earth 'didymia.'

Occurrence and separation v. NEODYMIUM. The metal, sp.gr. 6·4754; m.p. 940°, is obtained by the electrolysis of its fused chloride and purified by melting under anhydrous barium chloride in a magnesia crucible (Muthmann and Weiss, Annalen, 1904, 331, 1). It forms an ill-defined hydride.

Praseodymium carbide PrC_2, sp.gr. 5·10; closely resembles the neodymium compound, and is decomposed by water, yielding a mixture of acetylene, paraffins, and olefines.

Praseodymium fluoride PrF_3, yellow glistening crystals produced by mixing warm solutions of hydrogen fluoride and praseodymium nitrate (Ber. 1908, 41, 634).

Praseodymium chloride $PrCl_3$, pale green hygroscopic mass. Preparation, *v.* NEODYMIUM.

The heptahydrate separates in large green crystals (Scheele, Zeitsch. anorg. Chem 1898, 18, 352; Matignon, Compt. rend. 1902, 134, 427).

Praseodymium hydroxide $Pr(OH)_3$, a light green precipitate, thrown down by caustic alkalis or ammonia from soluble praseodymium slats. In the presence of hydrogen peroxide a hydrated praseodymium peroxide is formed (Chem. Zentr. 1902, i. 172).

Praseodymium peroxide PrO_2. The higher black oxide is produced on heating praseodymium hydroxide, nitrate or oxalate in the air, but its exact composition depends on the temperature. The maximum proportion of active oxygen is taken up when praseodymium nitrate is melted with potassium nitrate at 400°–450°. The presence of cerium increases the tendency to form the peroxide, whilst lanthanum and neodymium have an inhibiting action. The peroxide liberates iodine and chlorine from the corresponding halogen hydrides in aqueous solution. In acid solutions it oxidises cerous to ceric salts, and manganous salts to permanganic acid; with hydrogen peroxide it evolves oxygen (Monatsh. 1885, 6, 477; Zeitsch. anorg. Chem. 1898, 17, 310; *ibid.* 1902, 32, 1; 1904, 41, 94; Chem. Soc. Proc. 1901, 17, 66; Ber. 1892, 25, 569; 1902, 35, 2370, 3740).

Praseodymium oxide (*praseodymia*) Pr_2O_3, greenish-yellow powder, produced by heating the peroxide in hydrogen; it readily undergoes oxidation in the air, becoming brown.

Praseodymium sulphate $Pr_2(SO_4)_3,8H_2O$, monosymmetric crystals, isomorphous with the corresponding hydrated sulphates of neodymium, samarium and erbium (Zeitsch. Krist. 1901, 34, 307); it is the most stable hydrate, but two others are known with 12 and 15·5 H_2O.

Praseodymium nitrate $Pr(NO_3)_3,6H_2O$, deliquescent needles; forms well-defined double nitrates, *e.g.* $Pr(NO_3)_3,2NH_4NO_3,4H_2O$, and $Pr(NO_3)_3,2RbNO_3,4H_2O$ (Zeitsch. anorg. Chem. 1911, 69, 221).

Praseodymium carbonate $Pr_2(CO_3)_3,8H_2O$, forms green double carbonates with ammonium and potassium carbonates (Zeitsch. anorg. Chem. 1904, 41, 94).

Praseodymium oxalate $Pr_2(C_2O_4)_3,10H_2O$, crystalline pale green powder; the **acetylacetonate**, $Pr[CH(CO{\cdot}CH_3)_2]_3$, m.p. 146°, is bimolecular in boiling carbon disulphide.

Absorption spectrum of praseodymium consists of fine bands ranging from λ 597 to λ 444 (Annalen, 1890, 256, 159; Ber. 1892, 25, 569; 1900, 33, 42; Chem. Soc. Proc. 1898, 191, 71; *v.* NEODYMIUM).

Arc and spark spectrum v. NEODYMIUM.

Physiological action of praseodymium salts, *v.* NEODYMIUM. G. T. M.

PRECIOUS STONES are those minerals which, by reason of their high degree of hardness, brilliant lustre, and attractive colour, combined with rarity of occurrence, find an application in jewellery. The several kinds differ widely in chemical composition; but with the notable exceptions of diamond and turquoise, the majority of them fall in the oxide (including aluminate) and silicate divisions of the mineralogical system of classification. As indicating the range in composition, the following may be mentioned:—

Element: Diamond.

Sulphides: (Too soft; or affected by light. Pyrites is occasionally used in cheap jewellery).

Haloids: (Too soft. Fluor-spar has been used).

Oxides: Corundum (ruby and sapphire), quartz (including agate, amethyst, chalcedony, rock-crystal, jasper, &c.), opal, hæmatite.

Aluminates: Spinel, chrysoberyl ($BeAl_2O_4$).

Carbonates: (Too soft. Malachite and the satin-spar variety of calcite occasionally used.)

Sulphates: (Too soft. The satin-spar variety of gypsum and alabaster used for ornamental purposes.)

Phosphates: Turquoise, rarely lazulite and apatite.

Silicates: Beryl (aquamarine and emerald), felspar, garnet, jade, lapis-lazuli, olivine, rhodonite, spodumene, topaz, tourmaline, zircon, &c.

Organic compounds: Amber, jet.

For descriptions of each of these minerals, *see* under the respective headings; *see* also GEMS, ARTIFICIAL; GEMS, IMITATION AND COUNTERFEIT. L. J. S.

PRECIPITATE, RED, WHITE, *v.* MERCURY.

PREHENITENE *v.* CYMENES.

PREHENITOL *v.* PHENOL AND ITS HOMOLOGUES.

PRICEITE *v.* COLEMANITE.

PRICKLY COMFREY, *Symphytum asperrimum* (Donn). A succulent perennial plant which has been highly praised as a green fodder for farm animals. It is usually grown from root cuttings, and yields many crops per year. It should be cut before flowering and then has the composition (Kellner)—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
88·5	2·5	0·3	5·0	1·7	2·0

Only about 0·9 p.c. of digestible proteid is present. It can be made into hay, if cut while young. Kellner gives as the average composition of such hay—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
15·0	20·7	2·7	35·1	11·5	15·0

The protein includes 9·5 p.c. of digestible proteid. H. I.

PRICKLY PEAR, *Opuntia Tuna* (Mill.). A native cactus of the West Indies and Mexico, now introduced and become naturalised in many hot countries, in some of which, *e.g.* Cape Colony, New South Wales, St. Helena, it has become a troublesome weed. The fruit is sometimes eaten: according to König, it consists of—

Rind	Flesh	Seeds
36·5	60·2	3·3

and the flesh contains—

Water	Protein	Sugar	Sugar yielding carbohydrates	Fat	Ash
91·5	0·7	5·3	1·4	trace	0·3

Both the fruit and the 'leaves' are covered with sharp spines, which have to be removed before the fruit can be eaten. The succulent leaf-like branches, after the spines are removed by burning, can be used as food for animals in dry seasons, when green food is scarce. A specimen of these branches, grown in the Transvaal, was examined by the writer and found to contain (J. Agric. Science, 1908, 3, 29)—

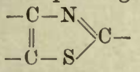
Water	Protein	Ether extract	N-free extract	Crude fibre	Ash
93·8	0·4	0·1	3·9	0·6	1·1

The ash was rich in potash and lime.

H. I.

PRIMROSE *v.* Triphenylmethane colouring matters.

PRIMULINE AND ITS DERIVATIVES (Syn. **Thiazol dyestuffs** or **Thiobenzenyl dyestuffs**). Under this heading will be considered the colouring matters characterised by the presence of the chromophoric grouping



which are derived from the condensation-products obtained by the action of sulphur upon paratoluidine and metaxylidine.

History. The preparation by Dahl and Co. (Eng. Pat. 14232, 1885) of a supposed thio-*p*-toluidine isomeric with the diaminoditolylsulphide of Merz and Weith led the writer in 1887 to study the action of sulphur upon *p*-toluidine. It was then found that if these substances were caused to react at the boiling-point in the proportion of 2 mols. of the latter to 4 atoms of the former, the loss of hydrogen sulphide which occurs corresponds with the equation :

$$2C_7H_7{\cdot}NH_2+S_4=C_{14}H_{12}N_2S+3H_2S.$$

The product obtained, which is now known as *dehydrothiotoluidine*, was a crystalline base forming long yellow needles of m.p. 191°, and b.p. 434°. It was insoluble in water, more readily soluble in alcohol, and formed sparingly soluble yellow salts. On treatment with fuming sulphuric acid it gave rise to a very sparingly soluble mono-sulphonic acid, characterised by forming a colourless sparingly soluble ammonium salt. Although the dehydrothiotoluidine contained only one diazotisable amino group, it was found that its diazo compound and also the diazo derivative of its sulphonic acid, when coupled with suitable amines and phenols (or sulphonic acids thereof) gave a series of colouring-matters which all dyed cotton directly without a mordant, this being the first known case of mono-azo dyestuffs having this property. Furthermore there was obtained, by the action of ammonia upon the diazotised dehydrothiotoluidine sulphonic acid, a bright greenish-yellow dyestuff also possessing a substantive affinity for cotton.

A further study of the action of sulphur upon *p*-toluidine revealed the fact that in addition to dehydrothiotoluidine there were also produced higher condensation-products of the latter, these compounds being formed according to the equations :—

$$3C_7H_7{\cdot}NH_2+S_8=C_{21}H_{15}S_2N_3+6H_2S$$

and $$4C_7H_7{\cdot}NH_2+S_{12}=C_{28}H_{19}S_3N_4+9H_2S$$

These more condensed bases (' primuline bases ') were obtained in larger amount by increasing the proportion of sulphur to 4½–5 atoms to 1 mol. amine. Although possessing in general properties similar to dehydrothiotoluidine, they are of a deeper yellow colour, more insoluble, and melt and boil at higher temperatures. Like dehydrothiotoluidine they contain a single diazotisable amino group and their diazo compounds upon combination with amine- and phenolsulphonic acids were found to produce azo- dyestuffs very similar to those derived from dehydrothiotoluidine and likewise possessing a direct affinity for cotton. In seeking for the cause of this affinity the discovery was made that the soluble alkaline salts of the monosulphonic acids of the above higher condensation products themselves dyed cotton directly, imparting thereto a primrose yellow colour. Furthermore, it was found that by immersing the cotton thus dyed in a weak solution of nitrous acid the amino group of the compound could be readily diazotised without disturbing the affinity of the compound for the fibre, and upon then bringing the cotton into a solution of an appropriate amine or phenol, a series of new dyestuffs were produced varying, according to the component used, from reddish-yellow to red, violet, and blue. These azo compounds being built up within the fibre substance, were fixed upon the cotton with a firmness far superior to that of the shades dyed with ordinary ' direct ' or ' salt ' colouring-matters, and possessed in consequence a high degree of fastness to washing, soap and alkalis.

Under the name of ' Primuline ' the sodium salt of the above-described sulphonic acid of the higher thionated *p*-toluidine was first manufactured and introduced into commerce by Messrs. Brooke, Simpson and Spiller, of London, in 1887, and employed for the production of so-called ' Ingrain Colours ' by the above process of diazotising and developing upon the fibre (A. G. Green, The Dyer, 1887, 7, 101 ; J. Soc. Chem. Ind. 1888, 7, 179 ; Chem. Soc. Trans. 1889, 55, 227). By reason of the fastness of the shades produced, more especially of the red obtained with β-naphthol, primuline at once acquired a high technical importance and was manufactured by various firms under the names of 'Polychromine,' 'Thiochromogen,' 'Sulphine,' ' Aureoline,' &c., all of which names have, however, now become obsolete.

The important principle of producing fast colours upon the fibre by dyeing with a substantive colouring-matter containing an amino group and afterwards diazotising and developing (' ingrain process ') has since been extended to a large number of other dyestuffs (Diaminogen, Diazo Blacks, Diamine Blacks and Blues, &c.), especially for dyeing fast navy blues and blacks.

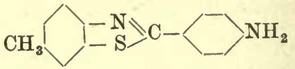
In addition to the colours produced upon the fibre from primuline by diazotisation and development, it was also found that a reddish-yellow of extreme fastness to light and washing was obtainable by oxidation of the dyed cotton with a solution of sodium or calcium hypochlorite. The application of the latter reaction to Primuline in substance, and to the sodium salt of dehydrothiotoluidine sulphonic acid, gave rise to valuable direct yellow dyestuffs fast to light (' Chloramine Yellow,' ' Oxyphenine,' ' Chlorophenine Yellow,' &c.). It was also found by Green and Evershed that the diazoamino compounds derived from Primuline or from dehydrothiotoluidine sulphonic acid or both, were substantive cotton dyestuffs possessing a bright greenish-yellow shade (' Thiazol

Yellow,' 'Clayton Yellow,' 'Turmerine'). These were first brought upon the market by the Clayton Aniline Co. and by Bayer & Co.

The trimethylammonium chloride of dehydrothiotoluidine, obtained by heating the base with methyl alcohol and hydrochloric acid was found by Green and Lawson (Ber. 1889, 22, 971) and by Rosenheck to be a valuable greenish-yellow basic dyestuff ('Thioflavine T'). Methylated derivatives of primuline were also introduced by Cassella & Co. as direct yellow dyestuffs for cotton under the name of 'Thioflavine S,' whilst the condensation product of primuline with formaldehyde was sold by Brooke, Simpson and Spiller for the same purpose.

The dehydrothioxylidine obtained by Schultz and Anschütz by heating *m*-xylidine with sulphur (Ber. 1889, 22, 582) was employed by the Berlin Aniline Co. for the preparation of a valuable pink cotton dyestuff ('Erica') by combination of its diazo compound with the α-naphthol-ε-disulphonic acid.

The constitution of dehydrothiotoluidine was investigated by P. Jacobsen (Ber. 1889, 22, 330); Gattermann (*ibid.* 1889, 22, 422); Anschütz and G. Schultz (*ibid.* 1889, 22, 580); A. G. Green (*ibid.* 1889, 22, 968; Chem. Soc. Trans. 1889, 55, 227); and Pfitzinger and Gattermann (Ber. 1889, 22, 1063). The last-named authors finally established its constitution as that of a *p*-aminobenzenyl-aminothiocresol (syn. *p*-aminophenyl-toluthiazol):

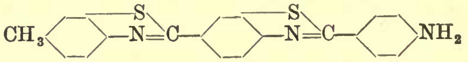


By deamination it was found to give rise to a benzenylaminothiocresol identical with that obtainable by oxidation of an alkaline solution of thiobenzoyl-*p*-toluidine

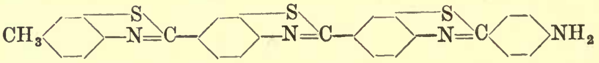
$$C_6H_5{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3.$$

It thus appears probable that in the action of sulphur upon *p*-toluidine the methyl group of the latter is first attacked with production of *p*-amino-dithiobenzoic acid $NH_2{\cdot}C_6H_4{\cdot}CS{\cdot}SH$, which reacts at once with the second molecule of *p*-toluidine giving the *p*-amino-thiobenzoyl-*p*-toluidine $NH_2{\cdot}C_6H_4{\cdot}CS{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3$. The latter is then converted into dehydrothiotoluidine by the withdrawal of 2 atoms of hydrogen as hydrogen sulphide.

Assuming that the further action of sulphur proceeds in a similar manner, the higher thionated bases will have the constitution:



and



Experiments conducted by the writer (unpublished) support the conclusion that commercial Primuline consists almost entirely of the mono-sulphonate of the first of these compounds. The latter also may sometimes be present to a small extent (as sulphonate), and is produced as chief product by heating dehydrothiotoluidine (2 mols.) with sulphur (4 atoms) (Green, Ber. 1889, 22, 970; Kalle & Co., D. R. P. 61204). In regard to the properties of these two bases it may be mentioned that the first melts at about 220°, is insoluble in alcohol, but soluble in nitrobenzene. The second melts at about 340°, and is insoluble in nitrobenzene, whilst its sulphonic acid has a more intense yellow colour than the sulphonic acid of the first.

Even with production of the tetranucleal base, the condensation by sulphur does not come to a stop, for upon heating *p*-toluidine with still more sulphur (3 atomic proportions to 1 mol. amine) products of extremely high melting-point are formed, which are solid at 300°, insoluble in all solvents, and not converted into soluble sulphonates even by highly fuming sulphuric acid.

Manufacture of Primuline and of dehydrothiotoluidine sulphonic acid. As the above-mentioned condensations proceed concurrently, it is not possible to obtain single products, but mixtures in different proportions of dehydrothiotoluidine with its higher thionated derivatives are always produced. Thus by reacting upon 2 mols. of *p*-toluidine with the following proportions of sulphur, the products consist of:—

With 4 atoms of sulphur	10 p.c. unaltered *p*-toluidine 50 p.c. dehydrothiotoluidine 40 p.c. primuline base
With 4½ atoms of sulphur	4 p.c. unaltered *p*-toluidine 33 p.c. dehydrothiotoluidine 63 p.c. primuline base
With 5 atoms of sulphur	2 p.c. unaltered *p*-toluidine 23 p.c. dehydrothiotoluidine 75 p.c. primuline base

The best proportions with respect to the quality of the Primuline obtained is that of 4½ atoms of sulphur to 2 mols. of *p*-toluidine. For the preparation of dehydrothiotoluidine base it is best to employ 2 atoms of sulphur to 2 mols. of *p*-toluidine and to subject the melt to a fractional distillation *in vacuô.* The excess of *p*-toluidine and a little diaminoditolyl sulphide pass over first and are then followed by pure dehydrothiotoluidine which crystallises on cooling.

The Primuline Melt is made in an enamelled iron pot of about 200 gals. capacity which is set in brickwork and provided with an enamelled iron agitator (*see* Fig. 1). The lid of the pot also carries a thermometer tube, and a hole for charging and emptying which is closed by a flange. Connected with the lid is a cast-iron pipe (preferably enamelled) of 8–10 ins. internal diameter and about 40–50 ft. long. This pipe is inclined upwards at an angle and serves as an air cooler to condense and return to the pot the *p*-toluidine which is carried off as vapour by the current of hydrogen sulphide. The whole or a part of the pipe can if necessary be cooled by a spray of water. From the further end a smaller pipe (2 ins. diam.) carries the gas, which should then be quite cold, to an iron box, in which a little p-toluidine collects, and thence it passes to the furnace where it is burnt under the pot, which it serves to heat.

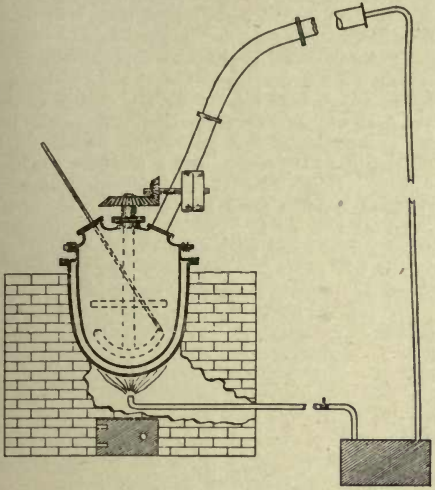


FIG. 1.

The pot is charged with 1000 lbs. of p-toluidine and 670 lbs. of sulphur. This is heated to the boiling-point for several hours, the temperature slowly rising as the reaction proceeds. The evolution of hydrogen sulphide commences at 170° and is completed when the temperature reaches 270°. The agitator is then stopped and the hot fluid is transferred from the pot under air pressure by means of a pipe inserted through the charging hole. After cooling and solidifying, the product is reduced to powder by means of a disintegrator. The yield is about 1125 lbs.

The Sulphonation is performed in an enamelled iron jacketted pan of 220 gals. capacity provided with cooling pipes through which cold water can be circulated (*see* Fig. 2). The contents of the pan can be rapidly stirred by means of an agitator, the blades of which pass between the loops of the cooling pipes.

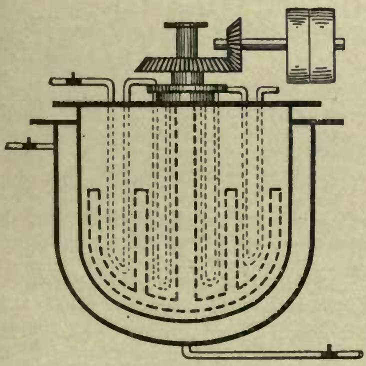


FIG. 2.

The ground melt (400 lbs.) is dissolved under rapid agitation in 1000 lbs. of 100 p.c. sulphuric acid (final temperature about 90°). There is then added slowly, while the mixture is kept rapidly agitated and well cooled, 800–900 lbs. of fuming sulphuric acid, 70 p.c. SO_3. The temperature is not allowed to rise above 40°, and the operation lasts about 6 hours. The sulphonation is complete when a small sample precipitated in water dissolves to a perfectly clear solution in boiling dilute ammonia. The mixture is then blown out of the pot by compressed air through the hollow spindle of the agitator and is run by means of a lead pipe into a wooden vat containing about 3000 gals. of cold water in which the dehydrothiotoluidine and primuline-sulphonic acids are thrown down as a voluminous orange-yellow precipitate. This is filtered off through a wooden filter-press in which it is thoroughly washed with water until all mineral acid is removed (*see* Fig. 3). In order to effect the separation of the dehydrothiotoluidine sulphonic acid from the primuline sulphonic acid, the sparing solubility of the ammonium salt of the former is made use of. The mixed sulphonic acids, in the form of the wet press cake, are stirred up with cold concentrated ammonia in a wrought-iron vessel provided with an agitator. The primuline dissolves whilst the ammonium dehydrothiotoluidine sulphonate separates out as a silky crystalline precipitate. The mixture is transferred to a suction filter and the precipitate washed with a little water until nearly white. Upon adding common salt to the filtrate, the primuline is thrown down as a dark yellow granular precipitate, which after drying is ground with sufficient common salt to bring it to standard strength. A small quantity which remains in the filtrate is recovered by adding the latter to the acid precipitating vat. The yield under the best conditions amounts to 530–560 lbs. of ammonium dehydrothiotoluidine sulphonate, and 1700–1800 lbs. of standard primuline, from 1000 lbs. of p-toluidine.

Application of Primuline (' **ingrain process** '). Primuline is chiefly employed in cotton dyeing, especially for dyeing fast reds upon cotton warps. It is also used to a smaller extent for dyeing silk. Owing to the want of fastness in the yellow condition, it is little used as a direct colouring-matter, but is employed almost exclusively for the production of various ingrain-colours by diazotisation and development on the fibre, the most important of these colours being the red obtained by combination with β-naphthol. The shades thus produced possess a high degree of fastness to soaping, milling, and acids, although not especially resistant to light. The following shades are obtained by development with the respective phenols and amines :—

Phenol $C_6H_5{\cdot}OH$	Yellow
Phenylmethylpyrazolone $C_3H_2N_2O(C_6H_5)(CH_3)$ . . .	Yellow
Resorcinol $C_6H_4(OH)_2$ . . .	Orange
2:3-Dihydroxyquinoline $C_9H_5N(OH)_2$	Orange
m-Phenylenediamine $C_6H_4(NH_2)_2$.	Reddish brown
m-Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$	Reddish brown
α-Naphthol $C_{10}H_7{\cdot}OH$ . . .	Maroon
β-Naphthol $C_{10}H_7{\cdot}OH$ . . .	Red
α-Naphthol-p-sulphonic acid $C_{10}H_6(OH)(SO_3Na)(1:4)$ . .	Crimson

β-Naphthol-di-sulphonic acid R, $C_{10}H_5(OH)(SO_3Na)_2(2:3:8)$	Maroon
α-Naphthylamine $C_{10}H_7 \cdot NH_2$	Purple
Hydroxy-α-naphthylamine methyl ether $C_{10}H_6(OCH_3)NH_2$	Reddish blue
2:3-Hydroxynaphthoic-anilide $C_{10}H_6(OH)CO \cdot NHC_6H_5$	Bordeaux
p-Amino-di-phenylamine $C_6H_5 \cdot NH \cdot C_6H_4 \cdot NH_2$	Olive green.

The reactions take place on the fibre with great ease and rapidity and follow the general equations for the formation of azo- dyestuffs :—

$$(a)\quad \underset{\text{(primuline)}}{P \cdot NH_2} + NO(OH) = \underset{\text{(diazo primuline)}}{P \cdot N_2 \cdot OH} + H_2O$$

$$(b)\quad \underset{\text{(diazo-prim.)}}{P \cdot N_2 \cdot OH} + \underset{\text{(phenol or amine)}}{HX(OH \text{ or } NH_2)} = \underset{\text{(ingrain colour)}}{P \cdot N_2 \cdot X(OH \text{ or } NH_2)} + H_2O$$

[In these equations, P stands for the radicle of Primuline $C_{21}H_{12}S_2(SO_3H)'$.]

The dyeing process is carried out as follows : The cotton is dyed from a boiling bath containing from 2–5 p.c. of the dyestuff together with an amount of common salt depending on the volume of the bath. It is then well rinsed in cold water to remove loose colour and steeped for one minute in a cold bath containing sodium nitrite (2½ p.c. on the weight of the cotton) and hydrochloric acid (7½ p.c.). The cotton is then again rinsed in water and brought into a cold bath containing the phenol or amine to be employed as developer, *e.g.* a solution obtained by dissolving one part of β-naphthol and one part of caustic soda in 400 parts of water. Phenols are employed in alkaline solution, amines in slightly acid solution.

In the dyeing of cotton warps the process is rendered very simple by employing a series of baths in line, through which the cotton passes continuously. The first bath contains a boiling solution of primuline, the second cold water for rinsing, the third a cold solution of nitrite and acid, and the fourth again cold water, the fifth is the developing bath and the last a final washing bath. The time of passage of the cotton through the entire series of baths is only from 3 to 5 minutes and the warp leaves fully dyed.

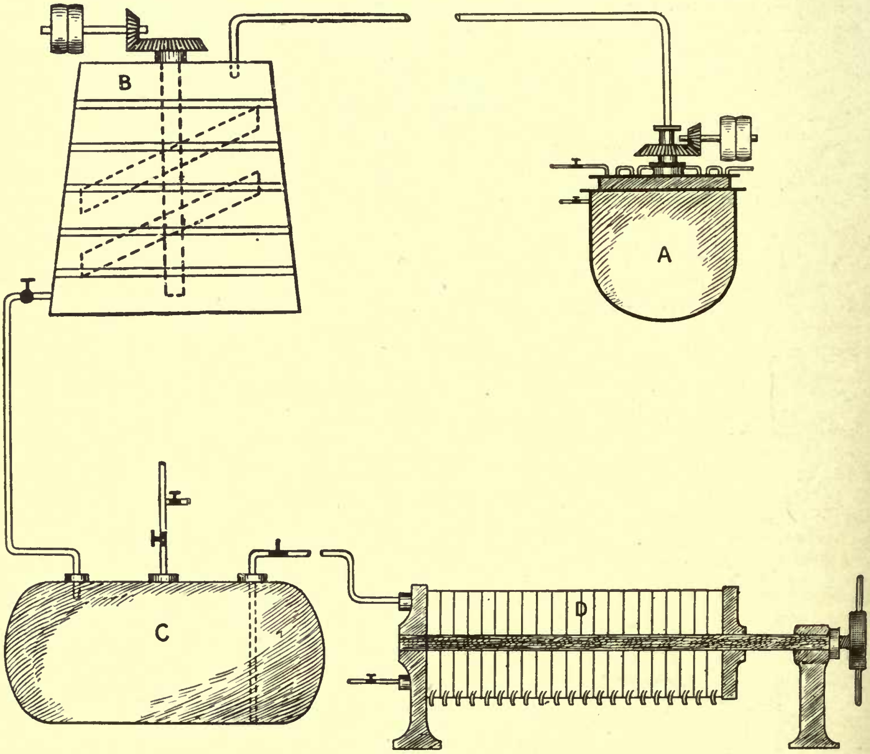


Fig. 3.

A fast orange-yellow, possessing a high degree of fastness to light, washing and other agents, is obtained by treating cotton dyed with primuline with a solution of calcium hypochlorite of about ¾°Tw. The reaction which occurs is probably as follows :

$$2P \cdot NH_2 + O_2 = P \cdot N : N \cdot P + 2H_2O$$

All the ingrain colours can be readily reduced to the original yellow primuline by boiling the dyed cotton for a few minutes in a solution of sodium hydrosulphite. The regenerated colour can then be rediazotised and again developed as desired.

In the diazotisation of primuline, care must be taken that the material is not exposed to strong light, as the diazo compound, although stable in the dark, is decomposed rapidly by sunshine according to the equation:

$$P{\cdot}N_2{\cdot}OH = P{\cdot}OH + N_2.$$

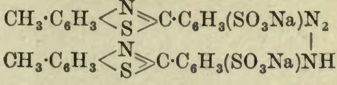
Nitrogen is evolved and the corresponding phenol is produced. This latter is of a pale yellow shade and no longer has the property of combining with phenols or amines to form azo colours. Upon this property has been based a process for producing coloured designs and photographic patterns upon textile fabrics, which is known as the 'diazotype process' (A. G. Green, C. F. Cross and E. J. Bevan, J. Soc. Chem. Ind. 1890, 9, 1001; Ber. 1890, 23, 3131; Eng. Pat. 7453, 1890). In this process, the material (cotton, silk, or paper) which has been dyed with primuline and diazotised, is exposed to light under the design or object which it is desired to copy, until the unshaded portion is no longer capable of combining with phenols. The material is then dipped or brushed with the developing solution when the pattern appears in the respective colour upon a pale yellow ground (*v.* PHOTOGRAPHY).

Clayton Yellow (Syn. Thiazol Yellow, Turmerine, Mimosa). These dyestuffs are mixtures of the diazoamino compounds, $D{\cdot}N_2{\cdot}NH{\cdot}D$, $D{\cdot}N_2{\cdot}NHP$, and $P{\cdot}N_2{\cdot}NH{\cdot}P$ (in which D and P respectively represent the radicles of dehydrothiotoluidine sulphonic acid and of primuline sulphonic acid).

They are prepared by the action of ammonia upon the diazo compounds of the above amine-sulphonic acids or by the combination of equimolecular quantities of the amine-sulphonic acids and their diazo- compounds (Clayton Aniline Co., Eng. Pat. 14207, 1889; Bayer and Co., Eng. Pat. 18354, 1889). The mixture of dehydrothiotoluidine sulphonic acid and primuline sulphonic acid, obtained by sulphonation of the crude primuline melt as above described, is suspended in water and neutralised with ammonia. To the solution of the mixed ammonium salts is then added one half of the quantity of sodium nitrite necessary for complete diazotisation (as determined by titration with a standard nitrite solution). Dilute hydrochloric acid is then run in until the mixture is acid to Congo paper. After stirring for half an hour to complete the diazotisation, sodium carbonate is slowly added during 2 or 3 hours until the mixture is just alkaline. After standing over-night, a further quantity of sodium carbonate is added and the mixture is slowly heated up to 70° by admission of steam. The colouring-matter is then salted out by addition of sufficient common salt, filtered off, dried and ground.

Clayton Yellow dyes cotton directly from a boiling bath in strong bright greenish-yellow shades, which render it valuable for admixture with other salt dyestuffs. It is, however, not fast to alkalis, acids or light. The dyestuff, both in substance and upon the fibre, is changed to orange-red by caustic alkalis. Hot aqueous acids decompose it with regeneration of the respective diazo compounds.

By employment of the pure ammonium salt of dehydrothiotoluidine sulphonic acid instead of the mixture with primuline, a greener brand of Clayton yellow is obtained, which has the constitution:—



$$\begin{array}{l} CH_3{\cdot}C_6H_3{<}\begin{smallmatrix}N\\S\end{smallmatrix}{\geqslant}C{\cdot}C_6H_3(SO_3Na)N_2 \\ \hspace{14em}| \\ CH_3{\cdot}C_6H_3{<}\begin{smallmatrix}N\\S\end{smallmatrix}{\geqslant}C{\cdot}C_6H_3(SO_3Na)NH \end{array}$$

Nitrophenine Yellow is a mixture of the compounds $D{\cdot}NH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$ and

$$P{\cdot}NH{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2,$$

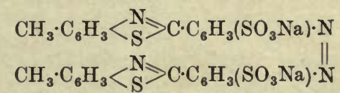
obtained by combining diazotised *p*-nitraniline with dehydrothiotoluidine sulphonic acid and primuline (Clayton Aniline Co., Eng. Pat. 24870, 1893).

A solution of *p*-nitrodiazobenzene chloride obtained by diazotising 180 lbs. of *p*-nitraniline by means of 100 lbs. of sodium nitrite and 43 gals. of hydrochloric acid is run slowly into a cold solution in about 1000 gals. of water containing the sodium salts of the mixed sulphonic acids, obtained by sulphonation of the crude primuline melt, in quantity equivalent to 98 lbs. of sodium nitrite, and rendered alkaline by addition of 300 lbs. of dry sodium carbonate. After stirring for some time the mixture is left over-night. It is then heated to about 80° by introduction of steam and the dyestuff salted out with common salt, pressed and dried.

Nitrophenine dyes cotton directly in pure yellow shades, which, however, are very deficient in fastness to light, alkalis and acids. Caustic soda changes the shade to violet. It is now but little used.

Chloramine Yellow (Syn. Oxyphenine, Diamine Fast Yellow B, Columbia Yellow). These dyestuffs are mixtures of the azo compounds, $D{\cdot}N_2{\cdot}D$, $D{\cdot}N_2{\cdot}P$, and $P{\cdot}N_2{\cdot}P$, prepared by oxidation with sodium hypochlorite of an alkaline solution of the mixed sodium sulphonates obtained from the crude primuline melt (Fr. Pat. 209519, 1890; Eng. Pat. 19061, 1891; 5761, 1892; 22914, 1884).

The dyestuffs, **Chlorophenine Y** and **Diamine Fast Yellow 2F**, are obtained in similar manner from the pure dehydrothiotoluidine-sulphonate, and therefore have the constitution:—

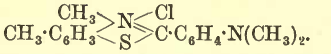


$$\begin{array}{l} CH_3{\cdot}C_6H_3{<}\begin{smallmatrix}N\\S\end{smallmatrix}{\geqslant}C{\cdot}C_6H_3(SO_3Na){\cdot}N \\ \hspace{14em}\| \\ CH_3{\cdot}C_6H_3{<}\begin{smallmatrix}N\\S\end{smallmatrix}{\geqslant}C{\cdot}C_6H_3(SO_3Na){\cdot}N \end{array}$$

For their preparation, 500 lbs. of ammonium dehydrothiotoluidine sulphonate is boiled in a lead-lined vat with 500 gals. of water containing caustic soda in small excess until all the ammonia has been expelled. When cold, the solution is diluted to 1000 gals. and 230 gals. of sodium hypochlorite solution (equals 10 p.c. active chlorine) are added. After standing over-night, the mixture is heated slowly by admission of steam, and is finally kept at 75°–80° until all chlorine has disappeared and the solution no longer reacts with starch iodide paper. The colour of the mixture is at first a dull yellow, but finally becomes a bright yellowish-orange. The colouring-matter is then salted out, pressed and dried.

It dyes cotton directly from a neutral bath in yellow shades which are unaffected by alkalis and acids and are extremely fast to light and chlorine. It is not discharged by reducing agents.

Thioflavine T (trimethyldehydrothiotoluidine chloride)



$$\overset{CH_3}{CH_3{\cdot}C_6H_3}\!\!<\!\!\overset{N<Cl}{\underset{S}{}}\!\!>\!C{\cdot}C_6H_4{\cdot}N(CH_3)_2.$$

Prepared by heating dehydrothiotoluidine base with methyl alcohol and hydrochloric acid for several hours under pressure at 160°–170° (A. G. Green and T. A. Lawson, Chem. Soc. Trans. 1889, 55, 230; Cassella & Co., Eng. Pats. 6319, 1888; 14884, 1888; J. Soc. Chem. Ind. 1890, 54; Dyers and Colourists, 1889, 106). In place of pure dehydrothiotoluidine, the mixture of this base with primuline base can be used, which is obtained by heating *p*-toluidine (2 mols.) with sulphur (4 atoms). In the latter case, dimethyl-primuline base is formed simultaneously and remains undissolved when the melt is extracted with boiling water. On adding salt to the hot solution, the dyestuff separates as a yellow crystalline precipitate. Thioflavine T is a basic colouring-matter which dyes tannin mordanted cotton in pure greenish-yellow shades. It also dyes silk a pure yellow with greenish fluorescence. It is faster than Auramine to acids, alkalis, and high temperatures, and since, like other members of the thiazol series, it is not affected by reducing agents, it also finds employment as a 'discharge' colour in calico-printing.

Thioflavine S is a dimethyl derivative of primuline obtained by the action of fuming sulphuric acid upon the portion insoluble in water of the product of methylation of crude primuline base (Cassella & Co., Eng. Pats. 6319, 1888; 14884, 1888; J. Soc. Dyers Cols. 1889, 106).

Thioflavine S dyes cotton directly in bright greenish-yellow shades, not affected by alkalis, although rather sensitive to light. It is fast to chlorine and is not discharged by reducing agents.

SUBSTANTIVE AZO DYESTUFFS DERIVED FROM DEHYDROTHIOTOLUIDINE SULPHONIC ACID AND FROM PRIMULINE.

The following compounds which dye cotton directly are prepared from the diazo derivatives of dehydrothiotoluidine sulphonic acid, or of the mixture of the latter with primuline, by combination with the respective components.

Dianil Yellow, $D{-}N_2{-}CH<^{CO{\cdot}CH_3}_{CO{\cdot}OC_2H_5}$, is obtained from the diazo derivative and acetoacetic ester (Eng. Pat. 17328, 1897).

Oriol Yellow (Syn. Cotton Yellow R, Alkali Yellow), $D{-}N_2{-}C_6H_3(OH)CO_2H$ is obtained from the diazo derivative and salicylic acid (D. R. P. 48465, 1888).

Benzo Brown 5R (Syn. Alkali Brown), $D{-}N_2{-}C_6H_3(NH_2)_2$ is obtained from the diazo derivative and *m*-phenylenediamine. It dyes cotton reddish-brown.

Atlas Red, $D{-}N_2{-}C_6H_2(CH_3)(NH_2)_2$ is obtained from the diazo derivative and *m*-toluylenediamine (Eng. Pat. 10448, 1890). Dyes cotton in terra-cotta shades, and gives browns upon diazotisation and development.

Cotton Yellow G,

$$D{-}N_2{-}C_6H(SO_3Na)_2(NH_2)_2$$

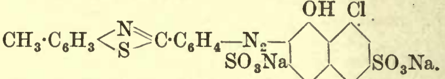
is obtained from the diazo compound and *m*-phenylenediamine-di-sulphonic acid (1 : 3 : 4 : 6) (Eng. Pat. 14678, 1893). It dyes cotton in orange-yellow shades.

Rosophenine 10B,

$$D{-}N_2{-}C_{10}H_5(OH)SO_3Na,$$

is obtained from the diazo derivative and α-naphthol-*p*-sulphonic acid (N. and W. acid). It dyes cotton in pink to red shades, fast to acids.

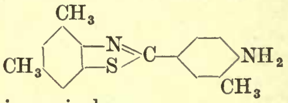
Diamine Rose,



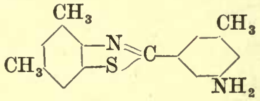
This dyestuff is obtained by combining the diazo compound of dehydrothiotoluidine (base) with 1 : 8-chloronaphthol-3 : 6-disulphonic acid. It dyes cotton directly in rose-pink shades.

SUBSTANTIVE AZO DYESTUFFS DERIVED FROM DEHYDROTHIOXYLIDINES.

By heating *m*-xylidine (6 parts) with sulphur (1 part) to the boiling-point until evolution of hydrogen sulphide ceases, a mixture is obtained consisting of dehydrothioxylidine,

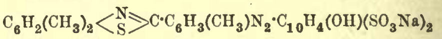


and the isomeric base,



The first forms small yellowish-white prisms of m.p. 107°, the second melts at 121°. After removal of the excess of *m*-xylidine by distillation, the two bases are separated by means of aqueous hydrochloric acid (30 p.c. HCl) in which the *iso*-base is insoluble (Anschütz and Schultz, Ber. 1889, 22, 582; Paul, Zeitsch. angew. Chem. 1896, 22; J. Soc. Chem. Ind. 1897, 730).

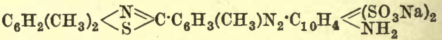
Erica B,



$$C_6H_2(CH_3)_2<^{N}_{S}>C{\cdot}C_6H_3(CH_3)N_2{\cdot}C_{10}H_4(OH)(SO_3Na)_2$$

is obtained by combining the diazo compound of dehydrothioxylidine with the α-naphthol-3 : 8-disulphonic acid (ε- acid) (Berlin Aniline Co., Eng. Pat. 1733, 1888). It dyes cotton directly in brilliant pink shades of good fastness to washing and fairly resistant to light.

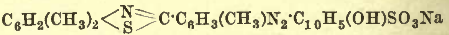
Salmon Red,



$$C_6H_2(CH_3)_2<^{N}_{S}>C{\cdot}C_6H_3(CH_3)N_2{\cdot}C_{10}H_4<^{(SO_3Na)_2}_{NH_2}$$

is obtained by combining the diazo compound of dehydrothioxylidine with β-naphthylamine-3 : 6-disulphonic acid (amino-R-acid). It yields bright salmon shades on unmordanted cotton. The Geranines also belong to the same class.

Emin Red,



$$C_6H_2(CH_3)_2<^{N}_{S}>C{\cdot}C_6H_3(CH_3)N_2{\cdot}C_{10}H_5(OH)SO_3Na$$

is obtained by combining the diazo- compound of *iso*dehydrothioxylidine with β-naphthol-6-sulphonic acid (Schaeffer acid). It dyes wool red from an acid bath but has little affinity for cotton.

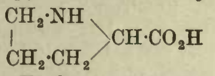
A. G. G.

PRINCE'S METAL or **PRINCE RUPERT'S METAL.** A brass containing about 25 p.c. of zinc.

PRINTER'S IRON LIQUOR. *Ferrous acetate* v. ACETIC ACID.

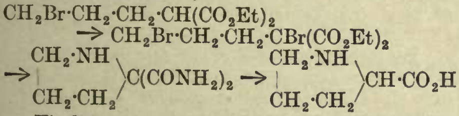
PRODUCER GAS v. FUEL.

PROLINE, *pyrrolidine-2-carboxylic acid*

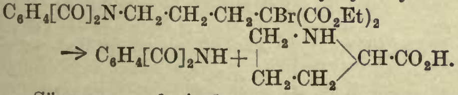


discovered by Fischer among the products of hydrolysis of casein (Zeitsch. physiol. Chem. 1901, 33, 151; Ber. 1902, 35, 227), is a common constituent of the product of proteid hydrolysis, occurring in quantities varying from 11 p.c. in salmin (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 407) to 1 p.c. and under in silk fibroin (Fischer, *ibid.* 1903, 39, 155; Abderhalden and others, *ibid.* 1909, 61, 259; 62, 129, 131, 142; 1910, 64, 460), v. PROTEINS. It has also been isolated from the etiolated seedlings of *Vicia sativa* (Linn.) and *Lupinus albus* (Linn.) (Schulze and Winterstein, *ibid.* 1905, 45, 38). It was shown by Fischer and Abderhalden (*ibid.* 1903, 39, 81; 45, 215), Fischer and Boehner (*ibid.* 1910, 65, 118) that proline is a primary product of protein hydrolysis, and not, as suggested by Sörensen (Chem. Zentr. 1905, ii. 398), a secondary product arising from α-amino-δ-hydroxyvaleric acid, since it is formed when the hydrolysis is effected by pepsin hydrochloric acid or pancreatin as well as by acids, caustic alkali, or barium hydroxide; whereas α-amino-δ-hydroxyvaleric acid has not been obtained by hydrolysis of proteins, and, moreover, does not yield proline by treatment with barium hydroxide.

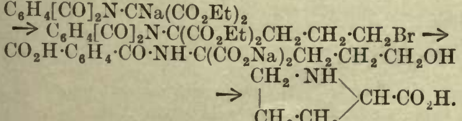
Synthesis.—Pyrrolidine-2-carboxylic acid was first synthesised by Willstätter (Ber. 1900, 33, 1160) from ethyl γ-bromopropylmalonate; this yields with bromine ethyl γ-bromopropylbromomalonate, which on treatment with ammonia and subsequent hydrolysis is converted into pyrrolidine-2-carboxylic acid



Fischer (Ber. 1901, 34, 454) obtained it in a similar manner from γ-phthaliminopropylmalonate; the bromo derivative of this compound when treated with ammonia gave a complex product from which phthalimide and pyrrolidine-2-carboxylic acid were obtained by hydrolysis



Sörensen and Andersen (Zeitsch. physiol. Chem. 1908, 56, 236), starting with ethyl phthaliminosodiomalonate, obtained a yield of 80 p.c. of proline by condensing the ester with trimethylene bromide, hydrolysing the ethyl γ-bromopropylphthaliminomalonate thus obtained with sodium hydroxide and evaporating the product with hydrochloric acid—



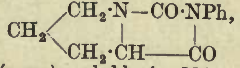
A further synthetic method due to Fischer and Zemplén (Ber. 1909, 42, 1022) consists in oxidising benzoylpiperidine with potassium permanganate into δ-benzoylaminovaleric acid $COPh\cdot NH[CH_2]_4CO_2H$, which with bromine and red phosphorus yields α-bromo-δ-benzoylaminovaleric acid, and this when boiled with hydrochloric acid yields proline in quantity.

The proline obtained from proteins is optically active and consists of a mixture of the lævo and racemic forms; the synthetic product is, of course, the racemic compound, but by a modification of the last method of synthetic preparation, Fischer and Zemplén (*ibid.* 2989) obtained both *d*- and *l*-proline, for this purpose *m*-nitrobenzoylproline obtained as above from *m*-nitrobenzoylpiperidine was resolved into its optically active constituents by means of the cinchonine salt, and these on hydrolysis with hydrochloric acid are decomposed into *m*-nitrobenzoic acid and the optically active prolines.

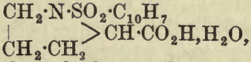
***l*-Proline,** the natural product, crystallises in flat needles, m.p. 206°–209°, with decomposition (Fischer, Zeitsch. physiol. Chem. 1901, 33, 151), 220°–222° (Kossel and Dakin, *ibid.* 1904, 41, 407), readily soluble in water or alcohol, insoluble in ether; it has a sweet taste; $[\alpha]_D^{20^\circ}$ −77·40° in aqueous solution. The synthetic preparation has m.p. 215°–220°, $[\alpha]_D^{20}$ −80·4° (±0·5°) (Fischer, Ber. 1909, 42, 2989). The *copper* salt $C_{10}H_{16}O_4N_2Cu$ forms large dark-blue soluble plates; l-*prolylchloride hydrochloride*

$$C_4H_8N\cdot COCl\cdot HCl$$

is prepared by the action of phosphorus pentachloride on *l*-proline (Fischer and Reif, Annalen, 1908, 363, 118); the *phenylisocyanate* yields the *anhydride* or *hydantoin*



m.p. 144° (corr.), soluble in 110 parts of hot water (Fischer, Zeitsch. physiol. Chem. 1901, 33, 151); the *β-naphthalenesulphonic derivative*



m.p. 133·7° (corr.); the anhydrous substance melts at 136°, soluble in 130 parts of boiling water; the *picrate* $C_{11}H_{12}O_9N_4$, m.p. 153°–154°, crystallises in needles from alcohol, and is less soluble than the corresponding salt of the racemic compound.

***d*-Proline** crystallises in prisms, m.p. 215°–220°, with decomposition, has $[\alpha]_D^{20^\circ}$ +81·9°; the *copper salt* closely resembles the corresponding salt of *l*-proline; the m-*nitrobenzoyl* derivative $C_{12}H_{12}O_5N_2$ has m.p. 137°–140°; $[\alpha]_D^{20^\circ}$ +120° (Fischer and Zemplén, Ber. 1909, 42, 2992).

***dl*-Proline** forms small prisms, m.p. 205° (with decomposition); and is converted by the action of putrefying bacteria into δ-aminovaleric acid (Ackermann, Zeitsch. Biol. 1911, 57, 104). The *copper salt* $C_{10}H_{16}O_4N_2Cu,2H_2O$, sky-blue plates or prisms, become violet when anhydrous; sparingly soluble in water, insoluble in alcohol; the m-*nitrobenzoyl* derivative has m.p. 90°–92° and is soluble in 40 parts of hot water; the *phenylisocyanate* derivative melts at about 170° with decomposition, forming the *hydantoin* $C_{12}H_{12}O_2N_2$, m.p. 118° (corr.) (Fischer, Ber.

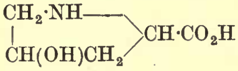
1901, 34, 454); the *picrate* $C_{11}H_{12}O_9N_4$, forms small yellow indefinite crystals, m.p. 135°–137°, readily soluble in hot water (Alexandroff, Zeitsch. physiol. Chem. 1905, 46, 17).

For the preparation and properties of polypeptides containing the *prolyl* radicle, *v.* Fischer and Abderhalden, Ber. 1904, 37, 3071; Fischer and Reif, Annalen, 1908, 363, 118; Fischer and Luniak, Ber. 1909, 42, 4752.

Estimation.—Proline occurs in that fraction of the esterified product of protein hydrolysis that is soluble in alcohol; and as it does not give up its nitrogen with nitrous acid as do the esters of the amino acids that distil over with it, the amount of proline present in the mixture is measured by the difference between the total nitrogen content of the mixture, and the nitrogen evolved on treating the mixture with nitrous acid (van Slyke, J. Biol. Chem. 1911, 9, 205).

Oxyproline, *hydroxyproline, hydroxypyrrolidine-2-carboxylic acid* $C_5H_9O_3N$ was isolated by Fischer (Ber. 1902, 35, 2660) from the hydrolysis product of gelatin, and is formed by the hydrolysis of other proteins (*cp.* Levene and Beatty, Zeitsch. physiol. Chem. 1906, 49, 252; Abderhalden, *ibid.* 1903, 37, 484, 499; Abderhalden and Rona, *ibid.* 1904, 41, 278).

The position of the hydroxyl group in the pyrrolidine ring has not been determined. Leuchs (Ber. 1905, 38, 1937) prepared synthetically two stereoisomeric γ-hydroxyprolines (4-*hydroxypyrrolidine-2-carboxylic acid*)



one of which is probably the racemic form of the natural hydroxyproline, but attempts to racemise the natural product in order to settle this point did not meet with success; and attempts to resolve the artificial acids were also unsuccessful (Leuchs and Felser, Ber. 1908, 41, 1726).

l-Oxyproline crystallises in colourless rhombic plates, m.p. 270°, with decomposition, readily soluble in water, less so in alcohol; it has a very sweet taste, $[\alpha]_D^{20°} - 81{\cdot}04°$. It is converted into *dl*-proline by reduction with hydrogen iodide and phosphorus. The *copper* salt

$$(C_5H_8O_3N)_2Cu,4H_2O$$

forms deep blue needles, readily soluble in water, insoluble in alcohol; the *phenyl*isocy*anate* $C_{12}H_{14}O_4N_2$ has m.p. 175°; the β-*naphthalene-sulphonic* derivative $C_{15}H_{15}O_5NS,H_2O$ becomes anhydrous at 85°, m.p. 91°–92° (corr.), soluble in 25 parts of hot water. M. A. W.

PROOF SPIRIT *v.* ALCOHOL.

PROPALDEHYDE $C_2H_5{\cdot}CHO$ is best prepared by the oxidation of propyl alcohol with chromic acid mixture (Marchionneschi, Gazz. chim. ital. 1907, 37, ii. 201; Lieben and Zeisel, Monatsh. 1883, 4, 14; Przybytek, J. Russ. Phys. Chem. Soc. 1876, 8, 335; Chancel, Annalen, 1869, 151, 301). It can also be obtained by heating propylene glycol with water at 220° (Linnemann, *ibid.* 1878, 192, 61), or together with acetone by using propylene dichloride (Linnemann, *ibid.* 1872, 161, 64). By the distillation of raw sugar with lime, propaldehyde is obtained, together with other products (E. Fischer and Laycock, Ber. 1889, 22, 105).

Properties. Propaldehyde is a liquid having a penetrating smell; b.p. 48·8° (corr.) (Linnemann, Annalen, 1872, 161, 22; *cf.* Rossi, *ibid.* 159, 79); sp.gr. 0·80648 at 15°, 0·79664 at 25° (Perkin, Chem. Soc. Trans. 1884, 476; *cf.* Brühl, Annalen, 1880, 203, 13; Pierre and Puchot, *ibid.* 1870, 155, 362; 1872, 163, 273); heat of combustion (const. press.) 434·35 cals. (Berthelot and Delépine, Compt. rend. 1900, 130, 1045); dielectric constant (Drude, Zeitsch. physikal. Chem. 1897, 23, 308); soluble in 5 vols. of water at 20°. By passing ammonia into a well-cooled solution of propaldehyde, *propaldehyde ammonia* is produced (Waage, Monatsh. 1883, 4, 708). Concentrated potassium hydroxide solution polymerises propaldehyde to *propionaldol* $CH_3{\cdot}CH_2{\cdot}CH(OH)CH(CH_3)CHO$ (Thalberg, *ibid.* 1898, 19, 154). Propaldehyde condenses with other aldehydes to form *aldols*, *e.g.* with acetaldehyde to yield the aldol

$$CH_3{\cdot}CH(OH)CH(CH_3)CHO$$

(Schmalzhofer, *ibid.* 1900, 21, 671; Kohn, *ibid.* 1901, 22, 21), but with formaldehyde the aldol is not obtained, the product being $\alpha\alpha$-dimethylolpropaldehyde

$$CHO{\cdot}CH(CH_3)CH_2{\cdot}OH$$

(Koch and Zerner, *ibid.* 443). By the action of aniline on a mixture of propaldehyde and acetaldehyde, $\alpha\beta$-dimethylquinoline, α-ethyl-β-methylquinoline, and quinaldine are formed (Rohde, Ber. 1887, 20, 1911). It combines with hydrogen cyanide to form α-hydroxybutyronitrile (α-cyanopropaldehyde) (Henry, Bull. Acad. roy. Belg. [iii.] 35, 133). Propaldehyde, sodium succinate, and acetic anhydride react at 110°–120°, yielding ethylparaconic acid (Fittig and Delisle, Annalen, 1889, 255, 56).

Detection. If propaldehyde is warmed with twice its volume of phenyl hydrazine, the product washed with dilute acetic acid and filtered, then, on heating with an equal quantity of zinc chloride at 180°, scatole is produced (E. Fischer, Ber. 1889, 22, 104).

Parapropaldehyde and **metapropaldehyde.** These two compounds, which each have the formula $C_9H_{18}O_3$, are produced by passing a few bubbles of hydrogen chloride through a solution of propaldehyde cooled in a freezing mixture. After standing for some time the metapropaldehyde, which is a light crystalline solid (m.p. 80°), is filtered off. The filtrate is distilled under 50 mm. pressure, and the parapropaldehyde obtained as a colourless liquid lighter than water; b.p. 85°–86°/50 mm.; 169°–170° (corr.), and changing at that temperature into propaldehyde. At −20° it solidifies to a mass of colourless needles. By heating either of these compounds with a little hydrochloric or sulphuric acid, propaldehyde is formed, together with a little tarry matter (Orndorff, Amer. Chem. J. 1890, 12, 352; Orndorff and Balcom, *ibid.* 1894, 16, 647). Parapropaldehyde is also formed by adding 200 grms. of ethyl chloracetate and some zinc to 100 grms. of propaldehyde, and allowing the mixture to stand for some months (Reformatsky, J. Russ. Phys. Chem. Soc. 1890, 22, 197). For action of bromine on parapropaldehyde, *v.* Franke, Annalen, 1907, 351, 421.

In these two polymerides union of the three molecules of propaldehyde probably takes place through the oxygen atoms, and metapropaldehyde and parapropaldehyde are probably examples of *cis-trans* isomerism (Orndorff and Balcom, *l.c.*).

PROPCESIN; PROPONAL *v.* SYNTHETIC DRUGS.

PROPIOLIC COMPOUNDS. From propiolic acid, $HC\vdots C\cdot COOH$, may be derived a series of acids of the general formula $C_nH_{2n+1}\cdot C\vdots C\cdot COOH$, and the members of this series may be regarded as the true homologues of propiolic acid, although the isomeric acids, in which the acetylene linkage is not in the α-β position, are often also described as propiolic compounds. The alkyl group may be replaced by an aromatic radicle, *e.g.* in phenyl propiolic acid $C_6H_5\cdot C\vdots C\cdot COOH$, the nitro-derivative of which is important as being the initial substance in Baeyer's original synthesis of indigo.

Alkylpropiolic acids $R\cdot C\vdots C\cdot COOH$. Methods of formation:

1. By the action of carbon dioxide on the sodium acetylenes—

$$R\cdot C\vdots CNa+CO_2=R\cdot C\vdots C\cdot COONa.$$

A convenient modification of this synthesis is to employ chlorocarbonic ester and saponify the product—

$$R\cdot C\vdots C\cdot Na+Cl\cdot COOC_2H_5=NaCl+R\cdot C\vdots C\cdot COOC_2H_5$$

(Moreu and Delange, Compt. rend. 1903, 136, 552).

2. By the action of dilute aqueous potash on the chloro derivatives of the acrylic acids—

$$R\cdot CCl:CH\cdot COOH-HCl=R\cdot C\vdots C\cdot COOH.$$

Reactions.—1. On reduction with sodium amalgam the corresponding fatty acid is obtained.

2. On boiling with alcoholic potash β-ketonic acids are formed—

$$R\cdot C\vdots C\cdot COOH+H_2O=R\cdot CO\cdot CH_2\cdot COOH$$

(Moreu and Delange, Compt. rend. 1902, 136, 733).

3. On heating with aqueous potash a ketone is obtained—

$$R\cdot C\vdots C\cdot COOH+H_2O=R\cdot CO\cdot CH_3+CO_2.$$

4. The propiolic esters react readily with alcohols and amines, forming addition compounds, and also with hydrazine forming pyrazole derivatives (Moreu and Lazennec, Compt. rend. 1906, 143, 596, and 1239).

Propiolic acid, propargylic acid,

$$H\cdot C\vdots C\cdot COOH,$$

was discovered by Bandrowski, who obtained it by warming the aqueous solution of the acid potassium salt of acetylene dicarboxylic acid. It is a colourless liquid, slightly heavier than water, with a strong smell of acetic acid, freely soluble in water and organic solvents, m.p. 9°, b.p. 140°–145° (decomposition). Propiolic acid is a stronger acid than acetic acid, which is attributed to the negative nature of the acetylene linkage. Its alkali and alkaline earth salts are characterised by excessive solubility in water; on boiling their solutions there is gradual decomposition

$$2HC\vdots C\cdot COOK=K_2CO_3+CO_2+2C_2H_2.$$

Owing to the fact that there is an acetylene hydrogen atom present, propiolic acid, its salts and esters are capable of forming characteristic metallic derivatives, such as

$$AgC\vdots C\cdot COOC_2H_5,\ CuC\vdots C\cdot COONa,\ \&c.$$

The copper compound on oxidation with potassium ferricyanide yields a propiolic derivative containing two acetylene linkages

$$(\cdot C\vdots C\cdot COOH)_2$$

and by the elimination of a carboxyl group and the subsequent oxidation of the copper compound of the substance thus obtained, Baeyer was able to perform a synthesis of the acid $(\cdot C\vdots C\cdot C\vdots C\cdot COOH)_2$, containing four acetylene linkages (Ber. 1885, 18, 2269).

Propiolic aldehyde $HC\vdots C\cdot CHO$ has been obtained by Claison (Ber. 1898, 31, 1022; 1903, 36, 3664) from the acetal of dibromoacrolein by converting it into propiolic acetal by the action of potash and then eliminating the ethoxyl group by means of dilute sulphuric acid. It is a colourless mobile liquid, b.p. 60°, with an even more pungent odour than acrolein. Like propiolic acid, it forms silver and copper derivatives. The aldehyde group is attached to the acetylene nucleus even less firmly than the carboxyl in propiolic acid, cold aqueous alkalis causing immediate decomposition—

$$HC\vdots C\cdot CHO+KOH=C_2H_2+H\cdot COOK.$$

Similarly hydroxylamine and phenylhydrazine do not condense normally, but yield cyclic products, namely isoxazole and pyrazole.

Methylpropiolic acid $CH_3\cdot C\vdots C\cdot COOH$, m.p. 76°, b.p. 203°. The esters of this acid and the higher homologues find some application in the preparation of artificial perfumes (Moreu, D. R. PP. 133631; 158252).

Phenylpropiolic acid $C_6H_5\cdot C\vdots C\cdot COOH$, has been obtained by the action of sodium and carbon dioxide on bromophenylacetylene, $C_6H_5\cdot C\vdots CBr$; by the action of carbon dioxide on sodium phenylacetylene $C_6H_5\cdot C\vdots CNa$; by the action of alcoholic potash on bromocinnamic acid or on phenyldibromopropionic acid. White crystals slightly soluble in water, m.p. 137°; it forms soluble salts, the sodium salt having strong disinfecting properties (Kozai, Chem. Zentr. 1906, i. 1758). Reactions: On heating it loses carbon dioxide and forms phenylacetylene; chromic anhydride oxidises it to benzoic acid; on reduction with zinc dust and acetic acid cinnamic acid is formed; bromine is added readily with the production of two isomeric dibromo-cinnamic acids; acetic anhydride causes condensation to a phenylnaphthalene derivative (Bucher, J. Amer. Chem. Soc. 1910, 32, 212).

***o*-Nitrophenylpropiolic acid**

$$C_6H_4(NO_2)\cdot C\vdots C\cdot COOH$$

(*see* INDIGO, ARTIFICIAL) was first obtained by Baeyer, who utilised it in the synthesis of indigo. On nitrating cinnamic acid the ortho-derivative is obtained; if this is converted into the dibromo acid by the addition of bromine and the product treated with alkali, *o*-nitrophenylpropiolic acid results (Baeyer, Ber. 1880, 13, 2258; D. R. P. 11857). On reduction in alkaline solution, it gives first isatogenic acid, and then loses carbon dioxide to form indigo; or by heating it may be converted by loss of carbon dioxide into *o*-nitrophenylacetylene, the copper compound of which may be oxidised by potassium ferricyanide to the diacetylene derivative, and this on reduction yields indigo. On treating with alkalis *o*-nitrophenylpropiolic acid forms isatin; by the action of concentrated sulphuric acid, isatogenic acid (Baeyer, D. R. P. 17656);

on treatment with sulphuric acid containing ferrous sulphate, indoin (Bayer, D. R. PP. 12601; 14997); by reduction with ammonium sulphide, indoxylic acid (*ibid.* 17656); by the milder reducing action of zinc and ammonium hydroxide, homo-anthroxamic acid (Heller and Tischner, Ber. 1909, 43, 4555).

PROPIONIC ACID $CH_3{\cdot}CH_2{\cdot}COOH$. Discovered by Gottlieb (Annalen, 52, 121) in 1844 by oxidising metacetone, and termed by him *metacetonic acid;* he also obtained it by heating gum, sugar, starch, &c., with concentrated potash solution. It is produced in the fermentation of calcium lactate, tartrate, and malate, and also in the fermentation of glycerol (Fitz, Ber. 12, 476), and is found among the products of the distillation of wood. It may be prepared by heating the nitrile with dilute sulphuric acid (Beckurts and Otto, Ber. 10, 262), or by treating propyl alcohol with a mixture of potassium chromate and sulphuric acid (Pierre and Puchot, Ann. Chim. Phys. [iv.] 28, 45). Colourless liquid smelling like acetic acid; b.p. 140·7°, sp.gr. 0·9937 at 20·3°/20·3° (Perkin, Chem. Soc. Trans. 1896, 1172). Soluble in water, but on addition of calcium chloride to the solution it separates out as an oil.

Methyl propionate boils at 79·5° (Kahlbaum, Ber. 1879, 344), and has sp.gr. 0·9387 at 0°/4° (Young and Thomas, Chem. Soc. Trans. 1893, 1219); **ethyl propionate** boils at 98·8°, and has sp.gr. 0·9124 at 0° (Schumann, Pogg. Ann. [2] 12, 41).

PROPOLIS (*Bee-bread, hive-dross;* Ger. *Vorwachs, Stopfwachs*). A resinous substance collected by bees from the young shoots of trees. It has a greyish-brown colour and an aromatic odour; m.p. 64°; sp.gr. 1·2 (Greshoff and Sach, Rec. trav. chim. 1903, 22, 139). It has been used in the treatment of rheumatism and gout (Brestowski, Handwörterbuch Pharm., II. 397).

Treatment with 95 p.c. alcohol extracts *propolis resin*, leaving *propolis wax* as residue. *Propolis balsam* is obtained from the resin by extraction with boiling light petroleum.

Commercial propolis is much adulterated with bees-wax, and by the addition of metallic and other heavy insoluble impurities, but the freshly-collected substance has approximately the composition: Loss at 100° (water and essential oils 5–6° p.c.; ash, 2·5 p.c.; insoluble residue, 12–13 p.c.; crude wax, 25–45 p.c.; propolis balsam 3 p.c.; propolis resin, 55–65 p.c. (Dieterich, Chem. Zeit. 1910, 34, 1006).

Propolis resin is a brownish-black substance of the composition $C_{26}H_{26}O_8$. It is soft and very aromatic, and has m.p. 66°–67° and sp.gr. 1·186. It is soluble in ether, chloroform, or hot alcohol. By prolonged heating at 100° it becomes much harder.

Propolis balsam is a syrupy, golden-yellow fluid, with a strong aromatic odour (Borisch, Pharm. Zentralhalle, 1907, 48, 929).

PROPYL. A monovalent radicle yielding two types of compounds:—

(*a*) $CH_3{\cdot}CH_2{\cdot}CHX$, *normal.*

(*b*) $(CH_3)_2CHX$, *iso.*

Propane $CH_3{\cdot}CH_2{\cdot}CH_3$ occurs in crude petroleum (Ronalds, Zeitsch. Chem. 1865, 523; Lefebvre, *ibid.* 1869, 185). Prepared by heating acetone, glycerol, propionitrile, or allyl iodide with hydriodic acid (sp.gr. 1·8) at 280° (Berthelot, Bull. Soc. chim. [ii.] 7, 60; 9, 13, 184); by the interaction of *iso*propyl iodide with zinc and dilute sulphuric acid (Schorlemmer, Annalen, 150, 209), or with zinc and absolute alcohol (Frankland, Chem. Soc. Trans. 1885, 238); by heating propyl or *iso*propyl iodide with aluminium chloride at 130°–140° (Köhnlein, Ber. 1883, 16, 561; L. Meyer, *ibid.* 1894, 27, 2766; Kluge, Annalen, 282, 229).

Propane is a colourless gas; heat of combustion (const. vol.) 528·4 Cal. (Berthelot and Matignon, Ann. Chim. Phys. [vi.], 30, 560), (const. press.) 553·5 Cal. (Berthelot, *l.c.*); ratio of specific heats 1·153 (Daniel, Bull. Soc. chim. 1899, [iii.] 21, 801); solubility in various solvents (Lebeau, Compt. rend. 1905, 140, 1454); illuminating power 1½ times that of ethane (Frankland, Chem. Soc. Trans. 1885, 239). Propane condenses to a colourless liquid; b.p. −37° (760 mm.); sp.gr. 0·536 at 0°/0°, 0·524 at 6·2°/6·2°, 0·520 at 11·5°/11·5°, 0·515 at 15·9°/15·9° (Hainlen, Annalen, 282, 245; L. Meyer, Ber. 1894, 27, 276; 1893, 26, 2071); b.p. −45° (1 atmo.), 0° (5 atmos.), 20° (8·8 atmos.), 43° (17·7 atmos.) (Olzewski, *ibid.* 1894, 27, 3306); b.p. −44·5° (757 mm.); crit. temp. 97·5°, crit. press. 45 atmos. (Lebeau, *l.c.*; Olzewski, *l.c.*; Hainlen, *l.c.*); remains liquid at −195°.

By the action of chlorine in the presence of iodine, the ultimate products are carbon tetrachloride and perchloroethane, formed by the action of excess of chlorine on the perchloropropane first formed (Krafft and Merz, Ber. 1875, 8, 1296).

Bromo Derivatives.

Propyl bromide, *α-bromopropane*

$$CH_3{\cdot}CH_2{\cdot}CH_2Br.$$

Prepared by the action of hydrobromic acid on propyl alcohol (Linnemann, Annalen, 161, 40).

B.p. 70·82° (corr.) (Brühl, *ibid.* 203, 13; *cf.* Zander, *ibid.* 214, 159); sp.gr. 1·3640 at 15°/15°, 1·3012 at 65·5°/65·5° (Perkin, Chem. Soc. Trans. 1896, 1237). By heating alone at 280°, or at a lower temperature with aluminium bromide, it is converted into *iso*propyl bromide (Aronstein, Ber. 1881, 14, 68; *cf.* Gustavson, J. Russ. Phys. Chem. Soc. 15, 61; Kekulé and Schrötter, Ber. 1879, 12, 2279); with aluminium bromide and benzene, cumene is formed (Gustavson, Ber. 1878, 11, 1251). Bromine alone yields propylene dibromide, whilst bromine and aluminium bromide yield dibromo-, tribromo-, and tetrabromopropanes (Mouneyrat, Compt. rend. 1898, 127, 273).

*iso***Propyl bromide,** *β-bromopropane*

$$CH_3{\cdot}CHBr{\cdot}CH_3.$$

Prepared by the action of hydrobromic acid on *iso*propyl alcohol at 150° (Linnemann, Annalen, 136, 41); by heating propyl bromide (*q.v.*) with aluminium bromide; by the action of bromine on *iso*propyl iodide (R. Meyer, J. pr. Chem. [ii.] 34, 105); by heating propylene dibromide with hydriodic acid at 150° (Linnemann, Annalen, 161, 57).

B.p. 59°–59·5° (740 mm.); sp.gr. 1·3097 at 20°/4° (Brühl, *ibid.* 203, 13; *cf.* Přibam and Handl, Monatsh. 2, 646; Zander, Annalen, 214, 160). Chlorine has no action in the cold; benzene and aluminium bromide yield cumene (Gustavson, Ber. 1878, 11, 1251).

Propylidene dibromide, *αα-dibromopropane* $CH_3{\cdot}CH_2{\cdot}CHBr_2$. Stated by Reboul (Ann. Chim. Phys. [v.] 14, 467) to be formed in small quantity together with propylene dibromide by the action of hydrobromic acid on α-bromopropylene; b.p. 130° (*circa*).

Propylene dibromide, *αβ-dibromopropane* $CH_3{\cdot}CHBr{\cdot}CH_2Br$. Prepared by the action of bromine on propylene (Reynolds, Annalen, 77, 120; Cahours, J. 1850, 496; Würtz, Annalen, 104, 244; Gladstone and Tribe, Chem. Soc. Trans. 1874, 408); by heating propyl bromide (Linnemann, Annalen, 161, 41; V. Meyer and Müller, Ber. 1891, 24, 4250), *iso*propyl bromide (Linnemann, Annalen, 136, 51), propyl or *iso*propyl chloride (Herzfelder, Ber. 1893, 26, 1260) with bromine in the presence of iron wire at 100°; together with trimethylene dibromide by heating propyl bromide and bromine at 45°–50° in the presence of aluminium bromide (Geromont, Annalen, 158, 370; Mouneyrat, Compt. rend. 127, 274).

B.p. 141·6° (corr.), sp.gr. 1·93326 at 20°/4° (Kahlbaum, Zeitsch. physikal. Chem. 26, 626, 646; *cf.* Zander, Annalen, 214, 175). At 240°–250° it is partly converted into trimethylene dibromide (2–3 p.c.) (Faworsky and Sokownin, *ibid.* 354, 325); bromine and aluminium bromide yield *ααβ*-tribromo- and *ααβγ*-tetrabromopropane (Mouneyrat, Bull. Soc. chim. [iii.] 19, 805); alcoholic potash gives two isomeric bromopropylenes, and with excess of potash allylene. Zinc and acetic acid or sodium amalgam and alcohol yield propylene (Linnemann, Ber. 1877, 10, 1111); hydriodic acid gives *iso*propyl bromide (*q.v.*). By heating propylene dibromide with water, hydrobromic acid, propylene glycol, and a trace of acetone are formed (Niederist, Annalen, 196, 358); with water and lead oxide, acetone, propionaldehyde and propylene glycol are the products (Eltekow, J. Russ. Phys. Chem. Soc. 10, 212); with water and silver oxide propaldehyde is formed, but not propylene glycol (Beilstein and Wiegand, Ber. 1882, 15, 1497).

Trimethylene dibromide, *αγ-dibromopropane* $CH_2Br{\cdot}CH_2{\cdot}CH_2Br$. Prepared by saturating allyl bromide with hydrogen bromide at 30°–35° (Bruylants, Bull. Acad. roy. Belg. 1908, 1085; *cf.* Erlenmeyer, Annalen, 197, 180; Lermontoff, *ibid.* 182, 358; Roth, Ber. 1881, 14, 1351), or by heating it with hydrobromic acid at 150° (Bogomoleta, Bull. Soc. chim. [ii.] 30, 23; *cf.* Geromont, Annalen, 158, 370); by heating trimethylene glycol with fuming hydrobromic acid at 100° (Freund, Monatsh. 2, 639). To purify the trimethylene dibromide from the propylene dibromide, which is also formed in small amount, Gustavson (J. pr. Chem. [ii.] 59, 303) fractionally treats the product with zinc in alcoholic solution, the propylene dibromide being much more readily attacked than the trimethylene dibromide.

B.p. 162·25°; sp.gr. 2·017 at 0°/0°, 1·987 at 17·5°/0° (Gustavson, *l.c.*); vapour pressures (Kahlbaum, Zeitsch. physikal. Chem. 26, 626). At 240°–250° it is converted mainly into propylene dibromide, traces of propyl and *iso*propyl bromides, and of tribromopropanes also being formed (Faworsky and Sokownin, Annalen, 354, 325). It yields trimethylene by the action of zinc dust and acetic acid (Zelinsky and Schlesinger, Ber. 1908, 41, 2429), or of zinc and alcohol (von Wolkow and Menschutkin, J. Russ. Phys. Chem. Soc. 30, 559; Ber. 1898, 31, 3070; Berthelot, Compt. rend. 129, 483; Gustavson, J. pr. Chem. [ii.] 36, 300). By heating with 12 parts of water at 170° propaldehyde, acetone, and trimethylene glycol are produced; with less water part of the propaldehyde is converted into methylethylacraldehyde, whilst with only 6 parts of water phorone and mesityl oxide are the products (Rix, Monatsh. 1904, 25, 267; *cf.* Niederist, *ibid.* 3, 838). By heating with silver oxide and water trimethylene glycol is formed (Beilstein and Wiegand, Ber. 1882, 15, 1497); sodium at 220° yields trimethylene. Alcoholic potash gives allyl bromide and ethyl allyl ether, whilst alcoholic ammonia in the cold yields trimethylene diamine. Aluminium bromide converts it into propylene dibromide (Gustavson, J. pr. Chem. [ii.] 36, 303).

Acetone dibromide, *ββ-dibromopropane, dibromoacetol* $CH_3{\cdot}CBr_2{\cdot}CH_3$. Prepared by the action of phosphorus tribromide (Linnemann, Annalen, 138, 125) or of phosphorus bromochloride (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48) on acetone; by treating β-bromopropylene with hydrobromic acid (Reboul, Ann. Chim. Phys. [v.] 14, 465); or similarly from allylene (Reboul, *l.c.*).

B.p. 114°–114·5° (740 mm.); sp.gr. 1·8149 at 0°/0°, 1·7825 at 20°/20°. Heated at 240°–250° it yields propylene dibromide and traces of trimethylene dibromide (Faworsky and Sokownin, Annalen, 354, 325). Alcoholic potash or potassium acetate gives hydrogen bromide and β-bromopropylene; water at 160° yields acetone; with zinc and acetic acid propane is the product (Linnemann, Annalen, 161, 67).

Higher brominated derivatives, v. Lespieau, Bull. Soc. chim. [iii.] 7, 260; Ann. Chim. Phys. [vii.] 11, 253; Mouneyrat, Compt. rend. 127, 274; Bull. Soc. chim. [iii.] 19, 805, 809; Gustavson, J. pr. Chem. [ii.] 46, 159; Reboul, Ann. Chim. Phys. [v.] 14, 476, 482; Berthelot and Luca Annalen, 101, 76; Wurtz, *ibid.* 104, 207; Tollens, *ibid.* 156, 168; Kronstein, Ber. 1891, 24, 4245; Oppenheim, Annalen, 132, 124; Pinner, *ibid.* 179, 60.

Chloro Derivatives.

Propyl chloride, *α-chloropropane*

$CH_3{\cdot}CH_2{\cdot}CH_2Cl$.

On chlorinating propane the chief product is propyl chloride, small quantities of higher chlorinated compounds also being formed (Schorlemmer, Annalen, 150, 209; 152, 159). Prepared by the action of iodine monochloride or of mercuric chloride on propyl iodide (Linnemann, *ibid.* 161, 37); by the interaction of propyl alcohol and hydrochloric acid or phosphorus pentachloride (Pierre and Puchot, *ibid.* 163, 266); by passing nitrosyl chloride into a toluene solution of propylamine at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431); by the action of hydriodic acid on epichlorhydrin (Silva, Compt. rend. 93, 739).

B.p. 44° (744 mm.) (Brühl, Annalen, 200, 179); 46·4°, sp.gr. 0·9156 at 0°, 0·8918 at 19·8°, 0·8915 at 39° (Pierre and Puchot, *l.c.*; *cf.* Linnemann, *l.c.*; Zander, Annalen, 214, 156; Schiff, *ibid.* 220, 98). By heating with iodine monochloride, carbon tetrachloride and perchlorethane are produced (Krafft and Merz, Ber. 1875, 8, 1296); with aluminium chloride, bromide or iodide propylene and hydrochloric acid are the products (Kerez, Annalen, 231, 306; Mouneyrat, Bull. Soc. chim. [iii.] 21, 616); with antimony pentachloride, propylene dichloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 161); with bromine and iron wire, propylene dibromide (Herzfelder, Ber. 1893, 26, 1260); with ethylamine, ethyl propylamine and ethyl dipropylamine (Arena, Chem. Zentr. 1907, ii. 1396).

*iso***Propyl chloride,** *β-chloropropane*

$CH_3{\cdot}CHCl{\cdot}CH_3$.

Prepared by the interaction of *iso*propyl iodide and mercuric chloride, or of propylene dichloride and hydriodic acid (Linnemann, Annalen, 136, 41); by passing nitrosyl chloride into a toluene solution of *iso*propylamine at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 30, 431).

B.p. 36·5°; sp.gr. 0·8588 at 20° (Zander, Annalen, 214, 157). Chlorine in the sunlight yields acetone dichloride and a trace of propylene dichloride, whilst iodine monochloride (Friedel and Silva, Zeitsch. Chem. 1871, 489) or antimony pentachloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 161; Silva, Compt. rend. 93, 739) give propylene dichloride. Heated with hydriodic acid, *iso*propyl iodide is produced; with bromine and iron wire, propylene dibromide (Herzfelder, Ber. 1893, 26, 1260); with ammonia, mono-, and di*iso*propylamines (Malbot, Bull. Soc. chim. [iii.] 4, 340, 632).

Propylidene dichloride, *αα-dichloropropane* $CH_3{\cdot}CH_2{\cdot}CHCl_2$. Prepared by the action of phosphorus pentachloride on propaldehyde (Reboul, Ann. Chim. Phys. [v.] 14, 458); b.p. 85°–87°; sp.gr. 1·143 at 10°. Alcoholic potassium hydroxide converts it into γ-chloropropylene, whilst antimony pentachloride yields *ααβ*-trichloropropane (Herzfelder, Ber. 1893, 26, 2434).

Propylene dichloride, *αβ-dichloropropane* $CH_3{\cdot}CHCl{\cdot}CH_2Cl$. Prepared by the action of chlorine on propylene (Cahours, Annalen, 76, 283; Reynolds, *ibid.* 77, 124); by heating propyl or *iso*propyl chloride with antimony pentachloride (Meyer and Müller, J. pr. Chem. [ii.] 46, 176); by the action of chlorine on propyl chloride in the presence of aluminium chloride (Mouneyrat, Bull. Soc. chim. [ii.] 21, 618); by heating allyl chloride and hydrochloric acid (Reboul, J. 1873, 321), or *iso*propyl chloride and chlorine (Friedel and Silva, Bull. Soc. chim. [ii.] 16, 3), in the latter case acetone dichloride also being formed.

B.p. 97·5°–98·5° (760·3 mm.) (Schiff, Ber. 1886, 19, 563); sp.gr. 1·1656 at 14°/14° (Linnemann, Annalen, 161, 62). Sodium amalgam or zinc and acetic acid are without action on propylene dichloride. Antimony pentachloride yields *ααβ*-trichloropropane, whilst chlorine in the presence of aluminium chloride gives *ααβ*- and *αββ*-trichloropropanes. Ten parts of hydriodic acid at 150° yield *iso*propyl chloride; twenty parts of water at 210°–220°, acetone and propaldehyde; lead oxide and water at 150°, propylene glycols; alcoholic potash, γ-chloropropylene together with a little β-chloropropylene.

Trimethylene dichloride, *αγ-dichloropropane* $CH_2Cl{\cdot}CH_2{\cdot}CH_2Cl$. Prepared by chlorinating trimethylene (Gustavson, J. pr. Chem. [ii.] 50, 380); by heating trimethylene dibromide with mercuric chloride (Reboul, Ann. Chim. Phys. [v.] 14, 460), trimethylene diiodide with water and silver chloride (Herzfelder, Ber. 1893, 26, 2434), or trimethylene glycol with fuming hydrochloric acid (Freund, Monatsh. 2, 638).

B.p. 125°; sp.gr. 1·1896 at 17·6°/4°. Alcoholic potassium hydroxide converts it into allyl chloride, whilst antimony pentachloride at 120° yields *ααγ*-trichloropropane.

Acetone dichloride, *ββ-dichloropropane, dichloroacetol* $CH_3{\cdot}CCl_2{\cdot}CH_3$. Prepared by the interaction of acetone and phosphorus pentachloride (Friedel, Annalen, 112, 236); of allylene and fuming hydrochloric acid (Reboul, Zeitsch. Chem. 1871, 704; J. 1873, 321); together with propylene dichloride by the action of chlorine on *iso*propyl chloride (Friedel and Silva, Zeitsch. Chem. 1871, 489; *cf.* Friedel and Ladenburg, Annalen, 142, 315).

B.p. 69·7° (corr.); sp.gr. 1·827 at 16° (Linnemann, *ibid.* 161, 67). With a deficit of alcoholic potassium hydroxide, hydrochloric acid and β-chloropropylene are produced, whilst with an excess, allylene is formed. Sodium at 130°–150° yields propylene (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48). By the action of 8 vols. of water at 160°–180° or of hydrochloric acid at 130°, acetone is produced. Antimony pentachloride yields *αββ*-trichloropropane (Herzfelder, Ber. 1893, 26, 1259).

Higher chlorinated derivatives: *v.* Friedel, Bull. Soc. chim. [ii.] 34, 129; Friedel and Silva, Zeitsch. Chem. 1871, 535, 682; Romburgh, Bull. Soc. chim. [ii.] 37, 103; Oppenheim, Annalen, 133, 383; Berthelot, *ibid.* 155, 108; Spring and Lecreiner, Bull. Soc. chim. [ii.] 48, 625; Borsche and Fittig, Annalen, 133, 114; Fittig and Pfeiffer, *ibid.* 135, 360; Hartenstein, J. pr. Chem. [ii.] 7, 313; Cahours, Annalen, 76, 283; Krafft and Merz, Ber. 1875, 8, 1296; Herzfelder, *ibid.* 1893, 26, 1258, 2435; Mouneyrat, Bull. Soc. chim. [iii.] 21, 619; Gustavson, J. pr. Chem. [ii.] 50, 381; Szenic and Taggesell, Ber. 1895, 28, 2667; Fritsch, Annalen, 297, 314.

IODO DERIVATIVES.

Propyl iodide, *α-iodopropane* $CH_3{\cdot}CH_2{\cdot}CH_2I$. Prepared by the action of iodine and red phosphorus on propyl alcohol (Chancel, Bull. Soc. chim. [ii.] 39, 648; *cf.* Linnemann, Annalen, 160, 240); b.p. 102·5°; sp.gr. 1·7829 at 20°/4° (Brühl, *ibid.* 203, 15; Dobriner, *ibid.* 243, 25; *cf.* Brown, Proc. Roy. Soc. 26, 238; Zander, Annalen, 214, 161). With aluminium iodide it yields propane, whilst with aluminium chloride or bromide propylene is the product (Kerez, Annalen, 231, 306).

iso-**Propyl iodide,** *β-iodopropane* $CH_3{\cdot}CHI{\cdot}CH_3$. Prepared by the action of hydriodic acid on propylene glycol (Würtz, Annalen, Suppl. 1, 381), glycerol (Erlenmeyer, Annalen, 126, 305; 139, 211; Markownikow, *ibid.* 138, 364), allyl iodide (Simpson, *ibid.* 129, 127), or *αβ*-propylene chloroiodide (Silva, Compt. rend. 93, 739; Sorokin, Zeitsch. Chem. 1870, 519); by the interaction of propylene and hydrogen iodide (Berthelot, Annalen, 104, 184; Erlenmeyer, *ibid.* 139, 228).

B.p. 89·5° (corr.); sp.gr. 1·7109 at 15°/15°

(Linnemann, *l.c.*; Brühl, *l.c.*; Brown, *l.c.*; Zander, *l.c.*). By heating in a sealed tube with water hydriodic acid and *iso*propyl alcohol are the products; with ammonia, mono*iso*propylamine; and with triethylamine, propylene and triethylammonium iodide (Reboul, Compt. rend. 93, 69; H. and A. Malbot, Bull. Soc. chim. [iii.] 4, 340, 632, 634). By interaction with magnesium, magnesium *iso*propyl iodide, propane, and propylene are formed (Tschelinzeff, J. Russ. Phys. Chem. Soc. 1904, 36, 549).

Propylene diiodide, *αβ-diiodopropane*

$CH_3\cdot CHI\cdot CH_2I$.

By the interaction of propylene and iodine (Berthelot and Luca, J. 1854, 453), or of allyl iodide and hydriodic acid (Malbot, Ann. Chim. Phys. [vi.] 19, 354); decomposes on distillation into hydrogen iodide and propylene. Sp.gr. 2·490 at 18·5°/18·5°; alcoholic potassium hydroxide converts it into propylene and iodine, whilst hydriodic acid yields *iso*propyl iodide.

Trimethylene diiodide, *αγ-diiodopropane* .

$CH_2I\cdot CH_2\cdot CH_2I$.

Prepared by the interaction of trimethylene glycol and fuming hydriodic acid at 100° (Freund, Monatsh. 2, 640), or of trimethylene dibromide and potassium iodide in alcoholic solution (Perkin, Chem. Soc. Trans. 1887, 13; Henry, Ber. 1885, 18, 519); b.p. 227° (decomp.), 168°–170°/170 mm.; sp.gr. 2·59617 at 4°/4°, 2·57612 at 15°/15°, 2·56144 at 25°/25°. With mercuric nitrite it yields *αγ*-dinitropropane (Keppler and Meyer, *ibid.* 1892, 25, 1709).

Acetone diiodide, *ββ-diiodopropane, diiodoacetol* $CH_3\cdot CI_2\cdot CH_3$. Prepared by the action of concentrated hydriodic acid on allylene (Oppenheim, Zeitsch. Chem. 1865, 719; Semenow, *ibid.* 725); b.p. 147°–148° (decomp.); sp.gr. 2·15° at 0° (Oppenheim), 2·4458° at 0° (Semenow). Volatile in steam; with alcoholic potassium hydroxide it yields hydriodic acid and *β*-iodopropylene, whilst silver oxide yields acetone (Sorokin, *ibid.* 1871, 264).

Hydroxy Derivatives.

Propyl alcohol, *α-hydroxypropane*

$CH_3\cdot CH_2\cdot CH_2\cdot OH$,

occurs in fusel oil from grain, potatoes, and beetroot (*v.* Fusel Oil). Formed in small quantities by the fermentation of glycerol by *Bacillus butylicus* (Fitz, Ber. 1880, 13, 1311; Morin, Bull. Soc. chim. 1887, [ii.] 48, 803). Prepared by heating allyl alcohol with potassium hydroxide (Tollens, Zeitsch. Chem. 1870, 457; 1871, 249); by reducing propaldehyde (Rossi, Annalen, 159, 80), or propionic anhydride (Linnemann, *ibid.* 148, 251; 160, 231; 161, 18) with sodium amalgam, or allyl alcohol with aluminium in 25 p.c. potassium hydroxide solution (Speranski, J. Russ. Phys. Chem. Soc. 1899, 31, 423); by the interaction of trioxymethylene and zinc ethyl and adding water to the product (Tischtschenko, *ibid.* 1887, 19, 483).

Colourless liquid; b.p. 97·19° (corr.) (Young and Fortey, Chem. Soc. Trans. 1902, 735), 16·2°/10·22 mm., 22·3°/16·78 mm., 31·4°/30·2 mm., 35·6°/39·6 mm., 43·2°/62·18 mm. (Kahlbaum, Ber. 1883, 16, 2480; *cf.* Richardson, Chem. Soc. Trans. 1886, 763; Konowalow, Pogg. Ann. [ii.] 14, 41); sp.gr. 0·81923 at 0°/4° (Young and Fortey, *l.c.*), 0·80804 at 15° (Doroschewsky and Roschdestvensky, J. Russ. Phys. Chem. Soc. 1909, 41, 1428; *cf.* Zander, Annalen, 224, 79; Brühl, *ibid.* 203, 268; R. Schiff, *ibid.* 220, 101); for table of sp.gr. of aqueous solutions, *v.* Doroschewsky and Roschdestvensky, *l.c.*; heat of combustion (Zoubow, J. Russ. Phys. Chem. Soc. 1898, 30, 926); dielectric constant (Philip, Zeitsch. physikal. Chem. 1897, 24, 18; Abegg and Seitz, *ibid.* 23, 309; Jahn, *ibid.* 1892, 10, 316; Eykmann, Rec. trav. chim. 1893, 12, 277); electric conductivity (Doroschewsky and Roschdestvensky, *l.c.*); absorption spectrum (Spring. Rec. trav. chim. 1897, 16, 1). Miscible with water in all proportions; on shaking repeatedly with calcium chloride and distilling the product, a crystalline compound $CaCl_2,C_3H_7OH$ remains (Göttig, Ber. 1890, 23, 181). Forms propoxides by replacement of the hydroxylic hydrogen by a metallic radicle. Oxidation with nitric acid yields carbon dioxide, oxalic acid, and propyl acetate (Klimenko, Ber. 1868, 1, 1604), whilst *Bacterium Aceti* (Brown), *B. Pasteurianum*, and *B. Kützingianum* yield propionic acid (Brown, Chem. Soc. Trans. 1886, 177; Seifert, Centr. Bakt. Par. 1897, 3, 337, 385). For products of oxidation obtained by passing vapour of propyl alcohol and air over a heated copper spiral, *v.* Orloff, J. Russ. Phys. Chem. Soc. 1908, 40, 203. By distillation with zinc, propylene and water are produced (Jahn, Ber. 1880, 13, 988); by slowly dropping propyl alcohol on to strongly heated zinc chloride, propylene, propaldehyde, and other products are formed (Le Bel and Greene, Amer. Chem. J. 1880, 2, 23). Chlorine in the cold yields *α*-chloropropaldehyde, *as*-dichloropropyl ether, and other products (Brochet, Compt. rend, 1895, 121, 648; *cf.* Oddo and Cusmano, Gazz. chim. ital. 1905, 31, i. 46), whilst bromine gives dibromopropaldehyde. Potassium hydroxide and iodine yield iodoform (Lieben, Annalen, Suppl. 7, 230), whilst with bromine propylbromal is the product. Methyl iodide and propyl alcohol at 218° yield *n*-propyl ether (Wolkow, J. Russ. Phys. Chem. Soc. 1889, 21, 338).

*iso***Propyl alcohol,** *β-hydroxypropane*

$CH_3\cdot CH(OH)CH_3$

occurs in fusel oil (*q.v.*). Prepared by reducing aqueous acetone (Friedel, Annalen, 124, 327; Linnemann, *ibid.* 136, 38) or propylene oxide (Linnemann, *ibid.* 140, 178) with sodium amalgam; by heating *iso*propyl iodide with water (Niederist, *ibid.* 186, 391), or better with the addition of lead hydroxide (Flawitzky, *ibid.* 175, 380); by the interaction of zinc methyl and *β*-iodoethyl alcohol (Butlerow and Ossokin, *ibid.* 145, 257); together with propyl alcohol by the action of nitrous acid on *iso*propylamine (Linnemann, *ibid.* 161, 43; *cf.* Ber. 1877, 10, 1111; Meyer, *ibid.* 1876, 9, 535).

Colourless liquid; b.p. 82·44° (corr.) (Young and Fortey, Chem. Soc. Trans. 1902, 735; Doroschewsky and Poljansky, J. Russ. Phys. Chem. Soc. 1910, 42, 1448; *cf.* Thorpe, Chem. Soc. Trans. 1897, 920); sp.gr. 0·80120 at 0°/4° (Young and Fortey, *l.c.*), 0·7982 at 4°/4°, 0·7903 at 15°/15° (Thorpe, *l.c.*; Louguinine, Ann. Chim. Phys. [vii.] 13, 289); for table of sp.gr. of aqueous solutions *v.* Doroschewsky and Poljansky, *l.c.*; critical temperature 234·9° (Pawlewsky, Ber. 1882, 15, 3035); heat of combustion (Zoubow, J. Russ. Phys. Chem.

Soc. 1898, 30, 926); dielectric constant (Loew, Ann. Physik. 66, 398; Drude, Zeitsch. physikal. Chem. 23, 39); absorption spectrum (Spring, Rec. trav. chim. 16, 1). Forms *iso*propoxides by replacement of the hydroxylic hydrogen by metallic radicles and yields a crystalline compound with calcium chloride. Chlorine converts *iso*propyl alcohol into *as*-tetrachloroacetone (Brochet, Ann. Chim. Phys. [vii.] 10, 134), whilst bromine yields *as*-tribromoacetone, acetone, and *iso*propyl bromide. Phosphorus trichloride yields di-*iso*propyl phosphite, *iso*propyl chloride, hydrogen chloride, and a small quantity of propylene (Milobdenski, J. Russ. Phys. Chem. Soc. 1898, 30, 730). Decomposes into propylene and water on heating with methyl iodide at 218° (Wolkow, *ibid.* 1889, 21, 337).

Propylene glycol, *αβ-dihydroxypropane*
$CH_3{\cdot}CH(OH)CH_2{\cdot}OH$.

Prepared by the interaction of powdered sodium hydroxide and glycerol, and subsequently distilling the product so formed (Morley and Green, Chem. Soc. Trans. 1885, 132); by reducing glycerol chlorhydrin with sodium amalgam (Lourenço, Annalen, 120, 91), or better by the action of acetyl bromide on glycerol, and reducing the compound thus formed with the zinc-copper couple and hydrochloric acid (Belohoubeck, Ber. 1881, 12, 1873); by heating 1 part of propylene dibromide with 26 parts of water (Niederist, Annalen, 196, 359); together with acetone and propaldehyde by the interaction of propylene dichloride or dibromide and water with lead oxide (Eletekow, J. Russ. Phys. Chem. Soc. 1878, 10, 210) or potassium carbonate (Hartmann, J. pr. Chem. 1897, [ii.] 55, 438); together with other products by the interaction of propylene dibromide and silver acetate (Wurtz, Ann. Chim. Phys. [iii.] 16, 383), or of allyl alcohol and 10 p.c. hydrochloric acid (Solonina, J. Russ. Phys. Chem. Soc. 1887, 19, 311).

Colourless liquid, having a sweet taste; b.p. 188°–189°; sp.gr. 1·051 at 0°, 1·0403 at 19·4° (Zander, Annalen, 214, 177); miscible with water or alcohol, soluble in 12–13 vols. ether. Oxidised by platinum black to lactic acid; by nitric acid to glycollic and oxalic acids; by chromic acid to acetic acid (Flawitzky, Ber. 1878, 11, 1256). Dilute sulphuric acid at 170° gives acetone, propaldehyde, and methylethylacraldehyde (Rix, Monatsh. 1904, 25, 267). Zinc chloride or dilute hydrochloric acid yield propaldehyde (Flawitzky, J. Russ. Phys. Chem. Soc. 1878, 10, 348; Linnemann, Annalen, 192, 61), whilst concentrated hydriodic acid yields *iso*propyl iodide. Either *sorbose bacterium* or *Mycoderma aceti* yields acetol (Kling, Compt. rend. 1901, 133, 231; 1899, 129, 1252; Bull. Soc. chim. 1901, [iii.] 25, 905), whilst *Bacterium termo* converts it into *l*-propylene glycol (Le Bel, J. 1881, 512). Bromine water yields acetol (Kling, Compt. rend. 1899, 129, 219; 128, 244). Sulphur chloride converts propylene glycol mainly into the chlorhydrin $CH_3{\cdot}CH(OH)CH_2Cl$, although small quantities of the isomeric compound $CH_3{\cdot}CHCl{\cdot}CH_2OH$ are probably also formed (Morley and Green, *l.c.*).

Trimethylene glycol, *αγ-dihydroxypropane* n-*propylene glycol*, $CH_2OH{\cdot}CH_2{\cdot}CH_2OH$, is a bye-product in the manufacture of soap-lye glycerin, and is formed by the fermentation of the bone fat (*v.* GLYCERIN; and Noyes and Watkins, J. Amer. Chem. Soc. 1895, 17, 890). Formed by the fermentation of glycerol by *Schizomycetes* in the presence of calcium carbonate (Freund, Monatsh. 1881, 2, 638). Prepared by heating trimethylene dibromide (i.) with water (Niederist, *ibid.* 1882, 3, 839); (ii.) with water and silver oxide (Beilstein and Wiegand, Ber. 1882, 15, 1497); (iii.) with potassium hydroxide (Zander, Annalen, 214, 178); or (iv.) with sodium acetate, and subsequently hydrolysing the diacetate thus produced with barium hydroxide (Reboul, Ann. Chim. Phys. 1878, [v.] 14, 491). According to Henry (Chem. Zentr. 1899, i. 968) the hydrolysis is best effected with powdered potassium hydroxide under reduced pressure. Colourless liquid; b.p. 210°; sp.gr. 1·0526 at 18°; miscible with water. By heating with sodium amalgam in amyl alcohol the monosodium derivative is formed, and on further treatment with metallic sodium this yields the disodium derivative (Parone, Boll. Chim. Farm. 1905, 44, 481).

Propyl cyanide, *butyronitrile*
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CN$.

Prepared by the interaction of ammonium butyrate and phosphorus pentoxide (Dumas, Annalen, 1847, 64, 334), or of acetonitrile, sodium, and ethyl iodide (Holtzwart, J. pr. Chem. 1889, [ii.] 39, 233); b.p. 116·3°–117°/750 mm.; sp.gr. 0·796 at 15° (van Erp, Rec. trav. chim. 1895, 14, 15). Reacts with sodium forming dimolecular propyl cyanide (iminobutyl propyl cyanide) (Wache, J. pr. Chem. 1889, [ii.] 39, 245). When administered to dogs it passes into the urine as ammonium thiocyanate (Lang, Arch. exp. Path. Pharm. 34, 247).

*iso***Propyl cyanide,** iso*butyronitrile*
$CH_3{\cdot}CH(CN)CH_3$.

Prepared by the interaction of *iso*propyl iodide and potassium cyanide (Markowinkow, Zeitsch. Chem. 1865, 107), or together with *iso*butyramide by the action of potassium thiocyanate on *iso*butyric acid (Letts, Ber. 1872, 5, 669); b.p. 107°–108°. By the action of sodium two bases, $C_{12}H_{22}N_2$ and $C_{19}H_{34}N_6$, are produced (Meyer, J. pr. Chem. 1888, [ii.] 37, 400).

Propyl *iso***cyanide,** *propyl carbylamine*
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NC$.

Prepared by the interaction of propyl iodide and silver cyanide; b.p. 97°–99° (Wade, Chem. Soc. Proc. 1900, 157).

*iso***Propyl** *iso***cyanide,** iso*propyl carbylamine* $CH_3{\cdot}CH(NC)CH_3$. Prepared by the interaction of *iso*propyl iodide and silver cyanide; b.p. 87°; sp.gr. 0·759 at 0° (Gautier, Ann. Chim. Phys. 1869, [iv.] 17, 249). Dilute hydrochloric acid converts it into *iso*propylformamide.

*iso***Propyl** *iso***cyanate,** iso*propyl carbimide* $CH_3{\cdot}CH(NCO)CH_3$. Prepared by the interaction of *iso*propyl bromide and silver cyanate, or by heating bromo-*iso*butyramide with dry sodium hydroxide; b.p. 67° (Hofmann, Ber. 1882, 15, 756).

Propyl thiocyanate $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}SCN$. Prepared by the action of potassium thiocyanate on propyl bromide in alcoholic solution; b.p. 163° (Schmidt, Zeitsch. Chem. 1870, 576).

*iso***Propyl thiocyanate** $CH_3{\cdot}CH(SCN)CH_3$. Prepared by the action of potassium thiocyanate on *iso*propyl iodide in alcoholic solution; b.p.

149°–151°; sp.gr. 0·963 at 20° (Henry, Ber. 1869, 2, 496; *cf.* Gerlich, Annalen, 178, 83; Ber. 1885, 8, 650).

Propyl *iso*thiocyanate, *propyl thiocarbimide, propyl mustard oil* $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NCS$. Prepared by the interaction of propylamine and carbon disulphide and subsequent treatment with mercuric chloride, followed by distillation in steam; b.p. 152·7°/743 mm.; sp.gr. 0·9909 at 0° (Hecht, Ber. 1890, 23, 282).

***iso*Propyl *iso*thiocyanate,** *iso**propyl thiocarbimide, iso**propyl mustard oil*

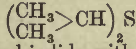
$CH_3{\cdot}CH(NCS)CH_3$.

Prepared similarly to the propyl compound (*v. supra*); b.p. 137°–137·5° (Jahn, Monatsh. 1882, 3, 168).

Propyl mercaptan $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}SH$. Prepared by the action of alcoholic potassium hydrosulphide on propyl bromide; b.p. 67°–68° (Roemer, Ber. 1873, 6, 784; Schatzmann, Annalen, 261, 7). Forms a mercury derivative $Hg(C_3H_7S)_2$, crystallising in plates, m.p. 68°.

***iso*Propyl mercaptan** $CH_3{\cdot}CH(SH)CH_3$. Prepared by the action of alcoholic potassium hydrosulphide on *iso*propyl iodide; b.p. 57°–60° (Claus, Ber. 1872, 5, 659; 1875, 8, 532). Forms a mercury derivative crystallising in plates. On oxidation with nitric acid the mercaptan yields *iso*propyl sulphonic acid.

Propyl sulphide $(CH_3{\cdot}CH_2{\cdot}CH_2)_2S$. Present in crude petroleum (Mabery and Smith, Amer. Chem. J. 1891, 13, 233; Ber. 1889, 22, 3303). Prepared by heating propyl chloride or iodide with alcoholic potassium sulphide; b.p. 141·5°–142·5°/772 mm. (Winssinger, Bull. Soc. chim. 1882, [ii.] 48, 109); sp.gr. 0·814 at 17° (Cahours, Compt. rend, 1873, 76, 133). Oxidised by nitric acid to propyl sulphoxide $(C_3H_7)_2SO_2$, which on treatment with potassium permanganate yields propyl sulphone, m.p. 29°–30° (Winssinger, *l.c.*). For compounds with platinum salts, *v.* Blomstrand, J. pr. Chem. 1888, [ii.] 38, 354, 498; Rudelius, *ibid.* 497, 508.

***iso*Propyl sulphide**  $\left(\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CH\right)_2S$. Prepared by heating *iso*propyl iodide with alcoholic potassium sulphide; b.p. 120·5°/763·1 mm. (Beckmann, *ibid.* 1878, [ii.] 17, 459). Oxidised by nitric acid to *iso*propyl sulphonic acid or by potassium permanganate to *iso*propyl sulphone, m.p. 36°. For compounds with platinum salts, *v.* Blomstrand, *l.c.*; Rudelius, *l.c.*

Propyl sulphite $(C_3H_7O)_2SO$. Prepared by the action of thionyl chloride on propyl alcohol; colourless liquid with an aromatic odour; b.p. 194°. Hydrolysed by 20 p.c. potassium hydroxide solution to potassium sulphate and potassium ethyl sulphonate after some months (Rosenheim and Sarow, Ber. 1905, 38, 1298).

Propyl sulphuric acid, *propyl hydrogen sulphate* $(C_3H_7)HSO_4$. Prepared by the action of sulphuric acid on propyl alcohol (Chancel, Compt. rend. 1853, 37, 410); an oil.

Propyl sulphate $(C_3H_7)_2SO_4$. Prepared by the action of chlorosulphonic acid on propyl alcohol (Mazurowska, J. pr. Chem. 1876, [ii.] 13, 162).

***iso*Propyl sulphuric acid** $(C_3H_7)HSO_4$. Prepared by the action of sulphuric acid on *iso*propyl alcohol or by the action of concentrated sulphuric acid on cardole (Spiegel, Chem. Zeit. 1895, 19, 1423); an oil.

Propyl nitrite $C_3H_7NO_2$. Prepared by heating propyl alcohol with amyl nitrite (Bertoni and Truffi, Gazz. chim. ital. 1884, 14, 23), or by passing nitrous fumes into propyl alcohol (Cahours, Compt. rend. 1873, 77, 745); b.p. 45°–46°; sp.gr. 0·935 at 21° (Cahours, *l.c*); b.p. 57° (Bertoni and Truffi, *l.c.*); sp.gr. 0·9881 at 0° (Přibram and Handl, Monatsh. 1881, 2, 655); mol. ref. (Brühl, Zeitsch. physikal. Chem. 1897, 16, 214).

***iso*Propyl nitrite** $C_3H_7NO_2$. Prepared by the action of silver nitrite on *iso*propyl iodide (Bevad, J. Russ. Phys. Chem. Soc. 1892, 24, 125; Silva, Bull. Soc. chim. 1869, [ii.] 12, 227); b.p. 39°–39·5°/752 mm. (Bevad, *l.c.*); b.p. 45°; sp.gr. 0·856 at 0°, 0·844 at 25° (Silva, *l.c.*). By passing hydrogen chloride into a cold ethereal solution, *iso*nitrosochloracetone and ammonium chloride are produced (Kiesel, J. Russ. Phys. Chem. Soc. 1895, 27, 119).

Propyl nitrate $C_3H_7NO_3$. Prepared by heating propyl alcohol with nitric acid in the presence of a small quantity of urea (Wallach and Schulze, Ber. 1881, 14, 421); b.p. 110·5°; sp.gr. 1·0747 at 5°, 1·0631 at 15°, 1·0531 at 25° (Perkin, Chem. Soc. Trans. 1889, 683); mol. ref. (Lowenherz, Ber. 1890, 23, 2181; Brühl, Zeitsch. physikal. Chem. 1895, 16, 214).

***iso*Propyl nitrate** $C_3H_7NO_3$. Prepared by heating silver nitrate with *iso*propyl iodide; b.p. 101°–102°; sp.gr. 1·054 at 0°, 1·036 at 19° (Silva, Annalen, 1870, 154, 256).

AMINES.

Propylamines. By the action of aqueous ammonia on propyl chloride (equal mols.) at 100°–110° for 10 hours, a mixture of monopropylamine (45 parts), dipropylamine (35 parts), and tripropylamine (20 parts) is obtained. These are separated by fractional distillation and purified as follows:—

(i.) To the *monopropylamine* ethyl oxalate is added with the formation of dipropyloxamide; (ii.) to the *dipropylamine* oxalic acid is added, dipropyloxamic acid being produced; (iii.) to the *tripropylamine* picric acid is added with the formation of the picrate (Chancel, Bull. Soc. chim. 1892, [iii.] 7, 405; *cf.* Malbot, Compt. rend. 1887, 104, 998; Vincent, *ibid.* 103, 208).

Propylamine, *a-aminopropane*

$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$.

Prepared as above, or by the reduction of ethyl cyanide with zinc and hydrochloric acid (Mendius, Annalen, 121, 133; Siersch, *ibid.* 144, 137; Silva, Zeitsch. Chem. 1869, 638; Linnemann, Annalen, 161, 44); by the action of bromine followed by potassium hydroxide on butyramide (Hofmann, Ber. 1882, 15, 769); by heating 10 parts of propyl nitrate with 19 parts of alcoholic ammonia at 100° (Wallach and Schulze, Ber. 1881, 14, 422); by fusing glycine ethyl ester with sodium hydroxide (Curtius and Gobel, J. pr. Chem. 1888, [ii.] 37, 163). B.p. 49°; sp.gr. 0·7330 at 4°, 0·7222 at 15°, 0·7144 at 25° (Perkin, Chem. Soc. Trans. 1889, 693); crit. temp. 218°, crit. press. 50 atmos. (Vincent and Chappuis, Compt. rend. 1886, 103, 379); elect. cond. (Oswald, J. pr. Chem. 1886, [ii.] 33, 361; Bredig, Zeitsch. physikal. Chem. 1894, 13, 295); mol. ref. (Brühl, *ibid.* 1895, 16, 214; Eykman, Rec. trav. chim. 1891, 12, 274).

Forms a hydrate and compounds with many metallic chlorides (Matthews, J. Amer. Chem. Soc. 1898, 20, 829; Skraup and Wiegmann, Monatsh. 1889, 10, 112; Hjostdahl, J. 1882, 476). The *platinichloride* has m.p. 214°; the *picrate*, m.p. 135° (Chancel, *l.c.*). Chromic acid oxidises propylamine to propionic acid (Chapman and Thorpe, Annalen, 142, 176); hydrogen peroxide yields at low temperatures a white crystalline peroxide (Kurovski and Nisenmann, J. Russ. Phys. Chem. Soc. 1911, 43, 654). Nitrous acid yields propyl and *iso*propyl alcohols and propylene (Meyer and Forster, Ber. 1876, 9, 535); nitrosyl chloride gives nitrosodipropylamine and dipropylamine hydrochloride (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431, 449).

Dipropylamine $(C_3H_7)_2NH$. For preparation *v. supra*; b.p. 109·4°–110·4°; sp.gr. 0·7524 at 4°, 0·7430 at 15°, 0·7357 at 25° (Perkin, Chem. Soc. Trans. 1889, 693); elect. cond. (Bredig, *l.c.*). Forms a hydrate which is a liquid, sparingly soluble in water. The *picrate* has m.p. 75° (Chancel, *l.c.*).

Tripropylamine $(C_3H_7)_3N$. For preparation, *v. supra*; b.p. 156·5°; sp.gr. 0·7563 at 18·2° (Roemer, Ber. 1873, 6, 1101); elect. cond. (Bredig, *l.c.*). Forms a hydrate which is a liquid, very sparingly soluble in water.

Tetrapropylammonium iodide $(C_3H_7)_4NI$. Prepared by the interaction of concentrated ammonia and propyl iodide at 150° (Malbot, *l.c.*; *cf.* Roemer, Ber. 1873, 6, 784); prismatic needles, somewhat soluble in water, more readily so in alcohol, but less so in ether. Silver hydroxide yields *tetrapropylammonium hydroxide* as a deliquescent mass (Roemer, *l.c.*).

*iso*Propylamines. *iso*Propyl iodide and an equivalent quantity of strong aqueous ammonia react very slowly at the ordinary temperature, but the product consists entirely of mono*iso*propylamine hydriodide. At higher temperatures the action is quicker, but di*iso*propylamine hydriodide, propylene, and ammonium iodide are also produced (H. and A. Malbot, Compt. rend. 1890, 111, 650; *cf.* Jahn, Monatsh. 1882, 3, 166). According to Zande (Rec. trav. chim. 1889, 8, 205) by heating 40 grms. of alcoholic ammonia (15 p.c. NH_3) with 40 grms. of *iso*propyl iodide at 100° for 4½ hours, a mixture of mono- and di-*iso*propylamine is obtained. The product is heated with a further quantity of *iso*-propyl iodide for ½ hour at 100°, and the di*iso*propylamine separated by conversion into the nitroso derivative. By the action of hydrochloric acid on *iso*propyl *iso*cyanide a mixture of the mono- and di*iso*propylamines is also obtained (Siersch, Annalen, 148, 263; *cf.* Gautier, Ann. Chim. Phys. [iv.] 17, 251).

***iso*Propylamine** $(CH_3)_2CH{\cdot}NH_2$. Prepared as above, or by the action of bromine followed by potassium hydroxide on *iso*butyramide (Hofmann, Ber. 1882, 15, 768); by reducing an alcoholic solution of acetonephenylhydrazone (Tafel, *ibid.* 1886, 19, 1926), acetoxime (Goldschmidt, *ibid.* 1887, 20, 728) or dihydroxyacetoxime (Piloty and Ruff, *ibid.* 1897, 30, 1664) with sodium amalgam. B.p. 33°–34° (Menschutkin, J. Russ. Phys. Chem. Soc. 1897, 29, 453); sp.gr. 0·690 at 18°; mol. ref. (Brühl, Zeitsch. physikal. Chem. 1895, 16, 214); elect. cond. (Bredig, *ibid.* 1894, 13, 295). Nitrous acid converts *iso*propylamine into *iso*propyl alcohol (Siersch, *l.c.*; Meyer and Forster, Ber. 1876, 9, 535); nitrosyl chloride yields nitrosodi*iso*propylamine and di*iso*propylamine hydrochloride (Solonina, J. Russ. Phys. Chem. Soc. 1898, 30, 431, 449). Forms compounds with metallic chlorides; the hydrochloride has m.p. 153°–155° (Skraup and Wiegmann, Monatsh. 1889, 10, 112).

Di*iso*propylamine $(C_3H_7)_2NH$. For preparation, *v. supra*; b.p. 83·5°–84°/743 mm.; sp.gr. 0·722 at 22°. The nitroso derivative

$$(C_3H_7)_2N(NO)$$

has m.p. 40°.

DIAMINES.

Propylene diamine, *αβ-diaminopropane*

$$CH_3{\cdot}CH(NH_2)CH_2{\cdot}NH_2.$$

Prepared by heating propylene dibromide and alcoholic ammonia at 100° (Hofmann, Ber. 1873, 6, 308); a strongly alkaline liquid, b.p. 119°–120°. The hydrochloride $C_3H_{10}N_2,2HCl$ has m.p. 220°. Propylene diamine forms compounds with numerous metallic salts (Werner, Zeitsch. anorg. Chem. 1899, 21, 200). *l*-Propylene diamine has been prepared by the resolution of the *dl*- base with *d*-tartaric acid; it has b.p. 121°; sp.gr. 0·8612° at 23°/4°; $[\alpha]_D -29{\cdot}65°$ (Tschugaeff and Sokoloff, Ber. 1909, 42, 55; 1907, 40, 3461; *cf.* Baumann, *ibid.* 1895, 28, 1180).

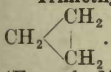
Trimethylene diamine, *αγ-diaminopropane* $CH_2(NH_2)CH_2{\cdot}CH_2{\cdot}NH_2$. Prepared by the interaction of trimethylene dibromide (1 part) and saturated alcoholic ammonia (8–9 parts) (Fischer and Koch, Ber. 1884, 17, 1799; Annalen, 1886, 232, 222; *cf.* Lellmann and Würthner, *ibid.* 1885, 228, 227); by the action of strong hydrochloric acid on trimethylene diphthalimide (Gabriel and Weiner, Ber. 1888, 21, 2670); by reducing *αγ*-dinitropropane with sodium amalgam and acetic acid (Keppler and Meyer, *ibid.* 1892, 25, 2638); b.p. 135°–136°/738 mm.; miscible with alcohol, ether, chloroform, or benzene. The hydrochloride $C_3H_{10}N_2,2HCl$ crystallises in large plates; on treatment with silver nitrite and water the hydrochloride yields allyl alcohol and other compounds (Demjanow, J. Russ. Phys. Chem. Soc. 1893, 25, 677).

Propylene $CH_3{\cdot}CH:CH_2$. Formed by passing the vapours of fusel oil (Reynolds, Annalen, 77, 118), petroleum (b.p. 60°–90°) (Prunier, J. 1873, 347), trimethylene (Tanatar, Ber. 1899, 32, 702, 1965), or other organic compounds through a red-hot tube; by distilling allyl iodide (Oppenheim, Annalen, Suppl. 6, 354). Best prepared by heating propyl alcohol with phosphorus pentoxide (Beilstein and Wiegand, Ber. 1882, 15, 1498) or by heating propyl or *iso*propyl alcohol with glacial phosphoric acid (Newth, Chem. Soc. Trans. 1901, 917). Also prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5 p.c. of anhydrous aluminium sulphate at 100°–110° (Senderens, Compt. rend. 1910, 151, 392); by heating *iso*propyl alcohol with fused zinc chloride (Friedel and Silva, J. 1873, 322); by the interaction of alcoholic potassium hydroxide with propyl iodide (Freund, Monatsh. 1882, 3, 633), or *iso*propyl iodide (Erlenmeyer, Annalen, 139, 228); by distilling glycerol with twice its weight of zinc-dust (Claus, Ber. 1885, 18, 2931); by heating allyl iodide with zinc and sulphuric acid or with mercury and hydrochloric acid (Berthelot and Luca, Annalen, 92, 309); by distilling allyl iodide (Linnemann, *ibid.* 161, 54; Gladstone and Tribe, Ber. 1873, 6, 1550; Niederist, Annalen, 196, 358), or allyl bromide (Wolkow and B. N. Menschutkin, J. Russ. Phys. Chem. Soc. 1898, 31, 3071) with zinc-dust in alcoholic solution; by the interaction of acetone dichloride (Friedel and Ladenburg, Zeitsch. Chem. 1868, 48) or acetone dibromide (Reboul, Ann. Chim. Phys. 1878, [v.] 14, 488) with sodium at 130°–150°; by the action of zinc ethyl on perchloromethane (Beilstein and Rieth, Annalen, 124, 242), bromoform (Beilstein and Alexejew, J. 1864, 470), or dichloroacetal (Paterno, Annalen, 159, 134); by fusing a mixture of calcium oxalate and potassium acetate (Dusart, *ibid.* 97, 127); by heating thymol with phosphorus pentoxide (Engelhardt and Latschinow, Zeitsch. Chem. 1869, 616).

Colourless gas, which can be liquefied under a pressure of 7–8 atmos. (Moltschanoffsky, J. Russ. Phys. Chem. Soc. 1889, 21, 32) or under atmospheric pressure by immersing in liquid air; b.p. −50·2° (Ladenburg and Krügel, Ber. 1899, 32, 1821). Heat of combustion (const. press.) 499·3 Cal. (Berthelot and Matignon, Bull. Soc. chim. 1894, [ii.] 11, 739). One vol. of water at $t°$ dissolves $0{\cdot}446506-0{\cdot}022075t+0{\cdot}0005388t^2$ vol. propylene (Than, Annalen, 123, 187); absolute alcohol dissolves 12–13 vols. One grm. of pure sulphuric acid absorbs 470 c.c. of propylene, forming the compound

$$[(CH_3)_2CH]_2SO_4$$

which on distillation with water yields *iso*propyl alcohol (Berthelot, Ann. Chim. Phys. 1895, [vii.] 4, 104). Oxidation with potassium permanganate or with chromic acid yields carbon dioxide and formic, acetic, and oxalic acids (O. and F. Zeidler, Annalen, 197, 249).



Trimethylene, cyclo*propane*, cyclo*trimethylene* $CH_2\langle CH_2 | CH_2$. Prepared by the action of sodium (Freund, Monatsh. 1882, 3, 626; *cf.* Reboul, Ann. Chim. Phys. 1878, [v.] 14, 488) or zinc (Gustavson, J. pr. Chem. 1887, [ii.] 36, 300) on trimethylene dibromide in alcoholic solution. According to Wolkow and B. N. Mentschutkin (Ber. 1898, 31, 3067) and Tanatar (*ibid.* 1899, 32, 702, 1965) the gas obtained by Gustavson's method always contains propylene; by passing the gas through bromine the propylene is absorbed and the trimethylene is obtained in a pure state. It has been shown, however, that the presence of propylene in the gas is due to the fact that trimethylene dibromide usually contains some propylene dibromide, and that if the trimethylene dibromide is quite pure, no propylene is obtained. If the first portion of the gas obtained by this method is rejected, the remainder is pure trimethylene (Gustavson, J. pr. Chem. 1907, [ii.] 76, 512; 1899, [ii.] 59, 302; Willstätter and Bruce, Ber. 1907, 40, 4456). Amyl alcohol may be substituted for ethyl alcohol in this preparation (Haehn, Arch. Pharm. 1907, 245, 518; Partheil, Verh. deut. Naturforsch. Aerzte, 1907, ii. 159).

Colourless gas, which can be liquefied under a pressure of 5–6 atmos. (Moltschanoffsky, J. Russ. Phys. Chem. Soc. 1889, 21, 32), or under atmospheric pressure by immersing in liquid air; it has also been solidified, m.p. −126°; b.p. −35° (*circa*) (Ladenburg and Krügel, Ber. 1899, 32, 1821). Heat of combustion (const. press.) 507·8 Cal. (Berthelot and Matignon, Bull. Soc. chim. 1894, [iii.] 11, 739). Trimethylene, when exposed to a red heat, remains unchanged, but at higher temperatures decomposes into ethylene, hydrogen, paraffins, and other products; by passing through a red-hot tube it is converted into propylene, but if air is present formaldehyde is produced (Tanatar, Ber. 1896, 29, 1297; and *l.c.*; Wolkow and B. N. Mentschutkin, *l.c.*; Berthelot, Compt. rend. 1899, 129, 483). At 100° in the presence of platinum black propylene is produced (Tanatar, Zeitsch. physikal. Chem. 1902, 41, 735), whilst with nickel reduction to propane is effected (Willstätter and Bruce, *l.c.*). One grm. of pure sulphuric acid absorbs 480 c.c. of trimethylene, yielding the compound $(CH_3{\cdot}CH_2{\cdot}CH_2)_2SO_4$, which on distillation with water gives propyl alcohol (Berthelot, Ann. Chim. Phys. 1895, [vii.] 4, 102). Chlorine reacts explosively in the sunlight, but in diffused daylight yields dichlorotrimethylene, trimethylene dichloride, β-chloropropylidene dichloride, and trichlorhydrin (Gustavson, J. pr. Chem. 1894, [ii.] 50, 381; 1890, [ii.] 42, 495). By the action of bromine trimethylene dibromide together with some propylene dibromide is formed; dry bromine acts very slowly, but if hydrogen bromide be present, the latter acts as a catalyst, greatly accelerating the reaction (Gustavson, *ibid.* 1899, [ii.] 59, 302; Compt. rend. 1900, 131, 233).

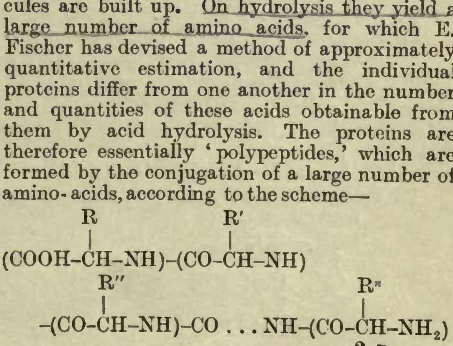
PROPYL ACETIC ACID *v.* VALERIC ACIDS.

PROPYLBENZENE *v.* CUMENES.

iso-**PROPYLSUCCINIC ACID** *v.* PIMELIC ACID.

PROTARGOL *v.* SYNTHETIC DRUGS.

PROTEINS. The chief nitrogenous constituents of both plants and animals are complex substances, forming a group to which at various times different names have been applied, such as albumens, albumenoids, and proteins (Ger. *Eiweiss-stoffe*, after a typical member of the group, egg-white). The class name now generally adopted is 'protein,' the terms 'albumen' and 'albuminoids' being employed to designate certain sub-groups. Altogether more than fifty proteins are known to occur naturally in plants and animals, which differ from one another in physical and chemical properties. It is only within the last few years that any definite knowledge as to their chemical constitution has been attained, and owing to the labours of Emil Fischer and his pupils, who have devised a systematic method of chemical examination, a fairly clear view is now obtainable of the way in which their highly complex molecules are built up. On hydrolysis they yield a large number of amino acids, for which E. Fischer has devised a method of approximately quantitative estimation, and the individual proteins differ from one another in the number and quantities of these acids obtainable from them by acid hydrolysis. The proteins are therefore essentially 'polypeptides,' which are formed by the conjugation of a large number of amino-acids, according to the scheme—



$$\mathrm{(COOH{-}\overset{\overset{R}{|}}{C}H{-}NH){-}(CO{-}\overset{\overset{R'}{|}}{C}H{-}NH)}$$
$$\mathrm{{-}(CO{-}\overset{\overset{R''}{|}}{C}H{-}NH){-}CO\ldots NH{-}(CO{-}\overset{\overset{R^n}{|}}{C}H{-}NH_2)}$$

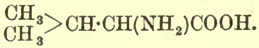
The following are the amino acids which have, up to the present, been isolated as hydrolysis products of the proteins :—

A. Monoamino carboxylic acids.

1. Glycine $C_2H_5NO_2$, or aminoacetic acid
$CH_2(NH_2)COOH$.

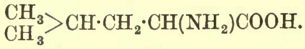
2. Alanine $C_3H_7NO_2$, or α-aminopropionic acid
$CH_3\cdot CH(NH_2)COOH$.

3. Valine $C_5H_{11}NO_2$, or α-amino*iso*valeric acid



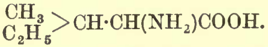
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH(NH_2)COOH.$$

4. Leucine $C_6H_{13}NO_2$, or α-amino-γ-methyl valeric acid



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\cdot CH_2\cdot CH(NH_2)COOH.$$

5. *iso*Leucine $C_6H_{13}NO_2$, or α-amino-β-methyl valeric acid



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH\cdot CH(NH_2)COOH.$$

6. Phenylalanine $C_9H_{11}NO_2$, or β-phenyl-α-aminopropionic acid
$C_6H_5\cdot CH_2\cdot CH(NH_2)COOH$.

7. Tyrosine $C_9H_{11}NO_3$, or β-parahydroxyphenyl-α-aminopropionic acid
$(OH)C_6H_4\cdot CH_2\cdot CH(NH_2)COOH$.

8. Serine, $C_3H_7NO_3$, or β-hydroxy-α-aminopropionic acid.
$CH_2(OH)CH(NH_2)COOH$.

9. Cystine $C_6H_{12}N_2O_4S_2$, or β-disulphido-α-aminopropionic acid
$COOH\cdot CH(NH_2)CH_2\cdot S\cdot S\cdot CH_2\cdot CH(NH_2)COOH$.

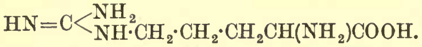
B. Monoamino dicarboxylic acids.

10. Aspartic acid $C_4H_7NO_4$, or aminosuccinic acid
$COOH\cdot CH_2\cdot CH(NH_2)COOH$.

11. Glutamic acid $C_5H_9NO_4$, or α-aminoglutaric acid
$COOH\cdot CH_2\cdot CH_2\cdot CH(NH_2)COOH$.

C. Diaminomonocarboxylic acids.

12. Arginine $C_6H_{14}N_4O_2$, or α-amino-δ-guanino-*n*-valeric acid



$$HN{=}C<\begin{matrix}NH_2\\NH\cdot CH_2\cdot CH_2\cdot CH_2CH(NH_2)COOH.\end{matrix}$$

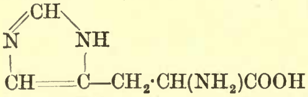
13. Lysine $C_6H_{14}N_2O_2$, or αε-diaminohexoic acid
$(NH_2)CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NH_2)COOH$.

D. Diamino - monohydroxymonocarboxylic acid.

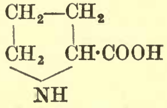
14. Caseinic acid $C_{12}H_{16}N_2O_5$, or diaminotrihydroxydodecanic acid

E. Heterocyclic compounds.

15. Histidine $C_6H_9N_3O_2$, or β-iminazole-α-aminopropionic acid (α-amino-β-glyoxaline-4(or 5)-propionic acid).

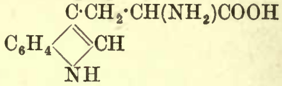


16. Proline $C_5H_9NO_2$, or pyrrolidine-2-carboxylic acid.



17. Oxyproline $C_5H_9NO_3$, or hydroxypyrrolidine-2-carboxylic acid, a hydroxyderivative of the above.

18. Tryptophan $C_{11}H_{12}N_2O_2$, or β-indole-α-aminopropionic acid



Other acids are probably obtainable by the hydrolysis of proteins which have not yet been isolated. In few cases have more than 70 p.c. of the theoretically obtainable amino acids been isolated from any given protein. Generally the yield is appreciably smaller. This is partly due to the imperfect methods of isolation of acids from the complex mixture which is formed in the hydrolysis, but partly probably also to the fact that other amino acids are obtainable, which have not yet been isolated in a pure state.

The quantitative estimation of the hydrolysis products. The method of isolating in an approximately quantitative manner the mono-amino acids derived from proteins is due chiefly to Emil Fischer. The protein is boiled with either sulphuric or hydrochloric acid ; as a rule, three times the weight of the latter acid of sp.gr. 1·19 is employed, and the heating is then continued until the biuret reaction (*see* below) has completely disappeared. The hydrolysis mixture is then concentrated *in vacuô* to a small volume, saturated with hydrochloric acid gas and allowed to stand for some days at 0°. The greater part of the glutamic acid then separates in the form of its hydrochloride. The filtrate from this substance is concentrated to syrup *in vacuô*, and the latter is then dissolved in absolute alcohol (3 litres for 1 kilo. of protein), and the alcoholic solution is saturated with hydrochloric acid gas. In this way the monoamino acids are esterified, but owing to the formation of water in the process, it does not proceed to completion at once. The alcohol is therefore distilled off in *vacuô*, and the residue is redissolved in alcohol, and the alcoholic solution is again treated with hydrochloric acid, and, after standing, concentrated. If glycine is present in any large quantity it separates at this stage. The esterification is, if necessary, repeated a third time. The esters of the hydrochlorides of the amino acids are finally obtained in the form of a thick syrup, from which the free esters must be prepared. This operation requires great care and skill, owing to the ease with which these substances are hydrolysed. The syrup is dissolved in about an equal volume of water, the solution cooled with ice and salt, and covered with a layer of ether. 33 p.c. caustic soda is then added in small quantities at a time, alternately with solid potassium carbonate, and the mixture is vigorously shaken after each addition, so that the amino acid esters, as they are set free from their hydrochlorides, are dissolved by the ether. As much caustic soda must be added as to combine with the whole of the hydrochloric acid and as much carbonate as will form a pasty mass, and the ether must be continuously poured off from the mass and renewed. The ether is then distilled off after drying the solution over anhydrous sodium sulphate, and the residual dark-coloured oil is subjected to fractional distillation *in vacuô* to separate as completely as possible the amino acids from one another. Modifications of the process of preparing the free esters from their hydrochlorides have been suggested, such, for example, as the treatment of the alcoholic solutions of the hydrochloride with the theoretical quantity of sodium ethoxide. The free esters are then distilled, first on a water-bath under a pressure of about 10 mm., such as can be produced by the ordinary laboratory water-pump, and afterwards under a pressure of 0·5 mm., which can be produced by a double Geryk pump worked by a motor; a liquid air trap is generally inserted between the pump and motor, to condense the volatile vapours. A good vacuum can also be produced by means of cocoa-nut charcoal cooled in liquid air. The following fractions are obtainable. Fraction I., b.p. under 40° at 10 mm. pressure; contains glycine and alanine. Fraction II., b.p. 40°–60° at 10 mm. pressure; contains alanine, leucine, and proline. Fraction III., b.p. 60°–90° at 10 mm. pressure; contains valine, leucine, proline. Fraction IV., water-bath, 100° at 0·5 mm. pressure; contains leucine and proline. Fraction V., oil-bath, 100°–130° at 0·5 mm. pressure; contains phenylalanine, aspartic acid, glutamic acid and serine. Fraction VI., oil bath, 130°–160°, contains also phenylalanine, glutamic and aspartic acids and serine. This fractional distillation of esters gives, therefore, only a very incomplete separation of the various amino acids. To get more complete separation the various fractions of the esters are hydrolysed, the lower fractions by water and the higher ones by barium hydroxide solution. The free acids obtained from the various fractions are separated from one another by a somewhat complex process of fractional crystallisation. The separation is rendered especially difficult by the fact that the amino acids, as they exist in the original protein, are optically active, and undergo partial racemisation during the process of hydrolysis. There are therefore present, in addition to the different amino acids, mixture of optical isomerides of the same acid. For these reasons it will be readily understood that a strict quantitative estimation of the various hydrolysis products has so far not been possible. These remarks apply more especially to valine, leucine and *iso*leucine. Certain of the other esters and acids have, however, special properties, which greatly facilitate their isolation. Thus proline, for example, is the only acid which is readily soluble in alcohol; the ester of phenylalanine can be readily separated from the other esters of the fraction in which it is contained by adding water and extracting the mixture with ether, when phenylalanine ester will be the only one dissolved; serine ester can be obtained by adding a small quantity of water to the fraction which contains it, and then adding to the mixture light petroleum, which causes the serine ester alone to separate. For details as to the methods of separation of the esters reference should be made to special text-books and monographs (*see* below).

Certain monoamino acids cannot be obtained in the form of amino acid esters that can be fractionally distilled, included amongst these are the important substances tyrosine, cystine, and tryptophan.

Tyrosine and cystine can be estimated by hydrolysing the proteins completely with hydrochloric acid, distilling off the greater part of the excess *in vacuô*, and then neutralising the residue. The two slightly soluble amino acids then crystallise out, and can be separated (but not quite quantitatively) from one another by fractional crystallisation from dilute ammonia. A simpler method of preparing cystine from wool, which gives a large yield of this substance on hydrolysis, has been suggested by Folin (Journal of Biol. Chem. 1910, 8, 9). The protein (the keratins, hair, and horn yield the largest amount of cystine) is hydrolysed with hydrochloric acid, and the mixture is then treated with solid sodium acetate until it is no longer acid to congo-red. On standing, cystine separates. It is recrystallised from 3 to 5 p.c. hydrochloric acid solution. The mother-liquor from cystine yields tyrosine. Tryptophan is usually destroyed during acid hydrolysis, and is therefore generally prepared from hydrolysis products which have been obtained by digestion with the enzyme trypsin (*see* below). As soon as the digestion mixture gives a maximal colouration when acidified and treated with bromine (which colour is due to tryptophan), it is acidified, boiled, filtered, sulphuric acid is added till 5 p.c. is present in the mixture, and then mercuric sulphate. The tryptophan is thereby precipitated as a mercury salt.

The diamino acids or hexone bases. These acids, arginine, lysine, and histidine, were, on account of their basic character, formerly known as the hexone bases, and, owing to the investigations of Kossel and Kutcher, fairly accurate methods exist for determining the amounts of these three substances, which are yielded by protein hydrolysis. The principle of the method of isolation consists in precipitating the bases from the acid solution of hydrolysis products by means of phosphotungstic acid, decomposing the phosphotungstates by baryta, and precipitating from the solution of free bases the arginine and histidine by silver sulphate and excess of barium hydroxide. From the filtrate of the silver salts of these two bases, the third base, lysine, can be precipitated either as phosphotungstate or as picrate. Arginine and histidine can be separated from one another by decomposing the silver salts, and then reprecipitating them from neutral solution by means of silver nitrate and barium carbonate. The histidine only is thereby precipitated and is filtered off; the silver salt of the other substance can only be made to come down from the filtrate when the latter is made strongly alkaline with baryta. From the respective fractions of silver salts arginine and histidine can be prepared pure in the form of picrolonates. By estimating the nitrogen in aliquot portions of the various fractions, the amounts of arginine, histidine, and lysine can be quantitatively determined. For details of the method reference must be made to special text-books.

Another method for estimating the diamino acids obtainable from proteins by hydrolysis is due to van Slyke. It can be carried out when only small amounts of material are available, and appears to be a relatively simple analytical process (Ber. 1910, 33, 3170; J. Biol. Chem. 1911, 9, 186; 10, 16).[1]

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[1] Since this article was written, van Slyke's method has been considerably extended. As it gives accurate

It will be seen from the above accounts that the methods of quantitatively separating the amino acids from one another are complex, and in the case of the mono-amino acids, at any rate, only approximately accurate. Nevertheless, the main chemical distinction between the various proteins depends on the quantities of the different amino acids that they yield on hydrolysis. This statement is illustrated by the accompanying table, which gives the percentage yields of the hydrolysis products obtained from certain typical proteins.

—	Salmine	Globulin (horse-blood)	Egg albumin	Serum albumin	Serum globulin	Edestin (hemp-seed)	Glutelin (wheat)	Gliadin (wheat)	Caseinogen (cow's milk)	Gelatin	Vitellin (egg)	Keratin (ox-horn)
Glycine . .	—	—	0	0	3·5	3·8	0·4	0·7	0	16·5	1·1	0·4
Alanine . .	—	4·19	2·1	2·7	2·2	3·6	0·3	2·7	0·9	0·8	+	1·2
Valine . .	4·3	—	—	—	+	+	—	0·4	1·0	1·0	2·4	5·7
Leucine . .	—	29·04	6·1	20·0	18·7	20·9	4·1	6·0	10·5	2·1	11·0	18·3
*iso*Leucine .	—	—	—	—	—	—	—	—	—	—	—	—
Phenylalanine.	—	4·24	4·4	3·1	3·8	2·4	1·0	2·6	3·2	0·4	2·8	3·0
Tyrosine .	—	1·33	1·1	2·1	2·5	2·1	1·9	2·4	4·5	0	1·6	4·6
Serine . .	7·8	0·56	—	0·6	—	0·4	—	0·2	0·23	0·4	—	0·7
Cystine . .	—	0·31	0·3	2·5	0·7	0·3	—	—	0·06	—	—	6·8
Proline . .	11·0	2·34	2·3	1·0	2·8	1·7	4·0	2·4	3·1	5·2	3·3	3·6
Hydroxyproline	—	1·04	—	—	—	2·0	—	—	0·25	3·0	—	—
Aspartic acid	—	4·43	1·5	3·1	2·5	4·5	0·7	1·3	1·2	0·6	0·5	2·5
Glutamic acid.	—	1·73	8·0	7·7	8·5	6·3	24·0	31·5	11·0	0·9	12·2	3·0
Tryptophan .	—	+	+	+	+	+	+	1·0	1·5	0	—	—
Arginine .	7·4	5·42	—	—	—	11·7	4·4	2·8	4·84	7·6	—	2·3
Lysine . .	0	4·28	—	—	—	1·0	2·2	0·0	5·80	2·8	—	—
Histidine .	0	10·96	—	—	—	1·1	1·2	1·2	2·59	0·4	—	—
Ammonia .	—	—	—	—	—	—	2·5	4·1	1·6	0·4	—	—

The numbers in the above table are due to various observers.

I. The Reactions of the Proteins.

The reactions which serve for the quantitative detection of the proteins may be divided into two classes, viz. precipitation reactions and colour reactions. The latter are due, for the most part, to individual amino acids, such as tryptophan, which can be obtained by hydrolysis of the proteins. As each amino acid is not contained in every protein, these colour reactions are not general.

Precipitation reactions. I. On heating many protein solutions, a precipitate or coagulum is formed, the process of production being known as coagulation. This phenomenon only takes place in the presence of water, and Chick and Martin (Journ. Physiol. 1910, 40, 404) have shown that it is due to a chemical reaction taking place between the protein and the water, and the rate of formation follows the ordinary laws of mass action. The temperature at which a coagulum forms was formerly regarded in the light of a physical constant, which could serve for the characterisation of individual proteins, in the same way that a melting-point can be used to characterise a simpler organic compound. In the course of the investigations just mentioned, however, it has been shown that a coagulum can be formed at different temperatures, but more rapidly at higher than at lower temperatures. The point of observed incipient coagulation will depend, therefore, on the rate at which the protein solution is heated. The observed coagulation point is also markedly affected by the physical and chemical character of the solution, especially the surface tension. It has been shown by Michaelis and Rona (Biochem. Zeitsch. 1910, 27, 38) that the optimum condition for the coagulation of a protein is when the protein and solution are isoelectric, *i.e.* when the surface-tension between the colloidal protein particles and the solution is at a maximum. This happens, in the case of dialysed egg-albumin and other proteins, when a small amount of acid has been added to the solution. For this reason, coagulation is generally carried out in solutions which have been slightly acidified with acetic acid, or with acid sodium phosphate. Chick and Martin have shown that coagulation can be best carried out in solutions which have been made distinctly acid to litmus paper by butyric acid (J. Physiol. 1911, 431). The presence of salt and other dissolved substances, in that these alter the physical character of the solutions, will also affect the coagulation point of the proteins. The heat coagulation is, perhaps, one of the most characteristic properties of large classes of proteins, although it can no longer be regarded in the light of a physical constant. II. Proteins can be precipitated from solution by various mineral acids. Nitric acid is generally employed; when allowed to flow on to the surface of a protein solution, it forms a white ring (Heller's test). Metaphosphoric acid (but not the ortho- or pyro- acids) is also a good precipitant. III. Ferrocyanic acid (a mixture of potassium ferrocyanide and acetic acid) is a good precipitant. Some proteins are soluble in excess of the reagent. IV. The salts of heavy metals precipitate proteins from solution. This

results with small amounts of material, it has proved a valuable process for characterisation of proteins. A very complete account of the method and its applications is given in Plimmer's 'Chemical Constitution of Proteins,' Part I., ed. 2, 1912, pp. 67 *et seq.*

reaction is very complex, and does not follow the ordinary mass reaction laws. When small quantities of salts of heavy metals are added to the solutions, either chemical action (formation of metallic salt of a protein) or physical absorption can take place according to the conditions of experiment. In the presence of larger quantities ordinary salt precipitation of proteins (*see* below) can take place. V. Proteins are precipitated by the ordinary alkaloidal reagents; such as phosphotungstic and phosphomolybdic acids, potassium mercuric iodide, potassium bismuth iodide, picric acid, and tannic acid. The last-named is perhaps the most widely used precipitant, and is generally employed in the form of the so-called Almen's reagent (4 grms. tannic acid in 8 c.c. 25 p.c. acetic acid +190 c.c. 40-50 p.c. alcohol). VI. Trichloracetic and sulphosalicylic acid are good precipitants. VII. Uranyl acetate precipitates proteins.

Colour reactions. I. Very dilute copper sulphate solution in the presence of sodium hydroxide and protein produces a reddish-violet to violet-blue colouration. This is generally known as the *biuret* reaction. II. On boiling proteins with nitric acid, yellow flakes or yellow solutions are formed, which on making alkaline become orange. This so-called *xanthoproteic* reaction is probably due to the presence of a benzene ring. III. By dissolving mercury in nitric acid without getting rid of the nitrous acid, the so-called *Millon's* reagent can be prepared. This solution gives with proteins a precipitate, which become pinkish on boiling. This reaction is due to the presence of tyrosine. IV. A large number of colour reactions are due to the presence of the tryptophan group and are in consequence not yielded by all proteins. The chief of these is the reaction of *Hopkins* and *Cole*, which is a modification of the earlier so-called *Adamkiewicz* reaction. A few drops of a solution of glyoxylic acid, prepared by reducing oxalic acid solution with sodium amalgam, are added to the protein solution, and then concentrated sulphuric acid is poured in; at the junction of the liquids a reddish-violet colour is produced in those proteins which contain a tryptophan group. Other reactions are Reichel's (blue colour with alcoholic solution of benzaldehyde, dilute sulphuric acid (1:1), and ferric chloride), and Rhode's (reddish to dark violet colour with dimethylaminobenzaldehyde and concentrated sulphuric acid). V. A series of reactions is given with several proteins, which is due to the presence of a carbohydrate group. In these cases it is not definitely proved whether the carbohydrate group is actually contained in the protein, or whether the latter is contaminated with a glyco-protein (*see* classification of proteins, below). The chief of these are the *Molisch-Udransky* reaction and *Bial's* orcin reaction. In the former, concentrated sulphuric acid is added to the protein solution containing a few drops of an alcoholic solution of α-naphthol; a violet colour is thereby produced which turns yellow on addition of sodium hydroxide or alcohol. Bial's reaction is carried out by the addition of dried protein to fuming hydrochloric acid; when solution has taken place after warming, a little solid orcinol and a drop of ferric chloride solution are added, and a green colour is produced. VI. On warming proteins containing sulphur with sodium hydroxide in the presence of a lead salt, a black colouration is produced showing the presence of cystine. VII. Diacetyl in the presence of potassium hydroxide solution gives a pink colour with proteins, accompanied sometimes with a fluorescence; the latter phenomenon disappears if the alkali be allowed to hydrolyse the protein before the addition of the diacetyl. The colour is due to the presence of a group—

$$NH:C(NH_2)NH{\cdot}R$$

(Harden and Norris, Journ. Physiol. 1911, 42, 332). VIII. Ruhemann has shown that triketohydrindene hydrate gives a blue colour with proteins, peptones and amino acids (Chem. Soc. Trans. 1910, 97, 2025). For conditions of reaction *v.* Aberhalden and Schmidt, Zeitsch. Physiol. Chem. 1911, 79, 37.

II. The Chief Physical Properties of the Proteins.

Colloidal nature. The most striking physical properties of the proteins may be attributed to their colloidal nature. Owing to the large size of the molecules of the majority of the proteins, they will not pass through animal and vegetable membranes, such as parchment paper, layers of collodion, 'sausage skin,' &c. They can consequently be readily separated from simpler substances by the process of dialysis. Owing to their ability to adsorb simpler substances, however, the last traces of the latter can be removed only with very great difficulty, and it has often been questioned whether the inorganic ash yielded by proteins after prolonged dialysis is not due to inorganic substances in actual chemical combination with the protein. Another method, analogous to dialysis for separating proteins from simpler substances is that of filtration under pressure through gelatin and collodion membranes. The former are hardened in formaldehyde before use, and the latter can be prepared from solutions of collodion either in acetic acid or alcohol and ether. Filtration can take place under either high or low pressures. In the former case, a Berkfeld or other similar filtering candle is employed, which is impregnated with gelatin solution and then formalised. In the latter case, filter-papers are impregnated *in vacuô* with either gelatin or collodion; the stronger the solution employed, the greater the pressure ultimately required for filtration. A special apparatus has been devised for the method of filtration by Bechhold, who has designated the process by the name of 'ultra-filtration.' The simpler molecules pass the filters, whereas the proteins remain behind.

Proteins can be carried out from solution by other colloids, and upon this property methods have been founded for separating proteins from solution. For this purpose two solutions have up to the present been chiefly employed, viz. mastic dissolved in 50 p.c. alcohol and dialysed ferric hydroxide. If these colloidal solutions be mixed with solutions not too rich in proteins, and some salt solution, such as that of magnesium sulphate, be added, the two colloids are precipitated together. In these cases the reaction is not always reversible, in that the protein cannot always be dissolved out from the precipitate by water; it can, however, be conveniently employed for separating proteins from solutions where they interfere with the reactions. Proteins can also be removed from solution by solid substances which act as absorbents, such as precipitated silicic acid, meerschaum, and iron oxide; under favourable conditions, this removal is complete. Proteins also, by virtue of their colloidal properties, can 'protect' other colloids and prevent the latter from being precipitated from solution. This property is best demonstrated by means of colloidal gold solutions. If an electrolyte be added to the bright-red colloidal gold solution, produced by the reduction of gold chloride by formaldehyde, a precipitate of the non-colloidal gold is produced. Zsigmondy has shown that proteins can inhibit this precipitation, and that the different members of the class show considerable variations with regard to the amount required to reveal this effect. He therefore has proposed to regard the quantity of a protein just necessary to inhibit the precipitation of gold from a certain standard colloidal solution by a definite amount of electrolyte as a factor which shall serve for the identification of individual proteins. This factor he designates the 'gold number' (Zeitsch. anal. Chem. 1901, 40, 697).

The solubility of the proteins and the salting out from solutions. The different proteins show great variations in the behaviour towards solvents. Some, such as keratin, horn, &c., are insoluble in all solvents; others, such as egg-albumin and serum albumin, are easily soluble (*i.e.* if not coagulated) in water, but insoluble in organic solvents. Other proteins, again, such as the globulins, are insoluble in pure water, but soluble in salt solutions when the latter are not too concentrated, and other proteins are soluble only in dilute acids or alkalis, such as the glutenins. All these kinds of proteins are insoluble in organic solvents. In addition there is a class of proteins which are insoluble both in water and absolute alcohol, but soluble in dilute alcohol (and also acetone). Certain plant proteins, known as the gliadins, possess this property. Aqueous solutions of proteins, furthermore, possess an important characteristic property. The majority of proteins can be precipitated from their aqueous solutions by the addition of salts. The precipitating power of salts varies greatly, and is an additive function, depending on both the acid and the base. Some salts will not precipitate at all, as the necessary concentration for precipitation is not attained when their saturation point is reached. The precipitation produced by salts is reversible, *i.e.* the precipitate redissolves on dilution of the solution. The proteins, furthermore, show great variation amongst themselves in the amount of salt necessary to precipitate them from solution. Thus, for example, the globulins are precipitated when their aqueous solutions are saturated by magnesium sulphate and half saturated with ammonium sulphate: the albumins, under these conditions, remain in solution. The method of salt precipitation of the proteins has been, therefore, extensively applied for the separation of proteins from solution, and from one another; in fact, it is the only general method which is available for the separation from one another of proteins which are soluble in water. It was employed by Denis as long ago as 1835, and but little progress has been made since the publication of Denis' monographs in 1856 and 1859 on the method of protein separation. The salts most commonly employed for precipitation are ammonium sulphate, magnesium sulphate, zinc sulphate, and (less frequently) sodium chloride. Limits of concentration can be experimentally determined at which protein precipitate begins and ends, and these limits will vary with the different proteins, and also (but to a lesser degree) with the concentration of the protein solution. The method of separation of proteins from one another by fractional salt precipitation is, however, far from efficient. If a salt be added to a mixture of proteins, as soon as the limit of concentration is reached at which the more readily precipitated protein falls out, precipitation will commence. The precipitate will contain, however, not only the protein of which the salt concentration limit has been reached, but some also of the less readily precipitable protein. The only method available, therefore, for separating water soluble proteins from one another is an imperfect one, and this fact accounts for a great deal of the uncertainty as to the homogeneity of a large number of proteins which have been submitted to investigation.

Reference has been already made to the co-precipitation of proteins by other colloids.

Crystallisation of proteins. A number of proteins are capable of existing in crystalline forms. The so-called aleurone grains found in plants and first observed by Hartwig in 1850 were subsequently shown to consist of proteins, and in 1877 Schmiedeberg succeeded in recrystallising the aleurone grains of Brazil nuts. Since that date several proteins have been obtained in crystalline form. The chief of these are serum and egg-albumins, and certain plant globulins (*see* below), of which edestin is a type. The conjugated protein hæmoglobin can also be obtained in crystalline form. Egg and serum albumins are obtained in crystalline form by mixing solutions of egg and serum proteins with an equal bulk of concentrated ammonium sulphate, filtering off the precipitated globulins, and then acidifying the filtrate, acetic acid being generally employed for this purpose in the case of egg-albumin, and sulphuric acid in the case of serum albumin. The plant proteins, such as edestin, can be obtained in a crystalline form by allowing the protein to separate out slowly from a not too concentrated (not more than 8 p.c.) saline solution, which had been previously warmed to 60°. 5 p.c. sodium chloride solution is generally employed. Many methods have been suggested for the preparation of hæmoglobin crystals. One of the most commonly adopted methods is that of diluting a hæmoglobin solution with one-fourth its volume of alcohol and cooling the mixture to 0°, when crystals separate out. There is a considerable literature dealing with the crystallisation of proteins, and much discussion as to the nature of the crystals, which do not behave entirely like those of simpler substances. It is also not known whether the natural proteins undergo any kind of chemical change during the course of crystallisation. In the case of egg-albumin, it has been thought that the crystallised protein is a salt, and its 'gold number' (see above) differs very appreciably from that of the non-crystallised protein.

Other physical properties of the proteins. Few of the other physical properties can be regarded as typical of individual proteins. Their solutions are optically active, being lævo-rotatory with the exception of hæmoglobin, which, according to Gamgee and Croft-Hill, is slightly dextro-rotatory ($[a]_D = +10{\cdot}4°$). The number of reliable determinations is small; others contain considerable sources of error, for, as the molecular weight is large, very small quantities of either acid or alkali may convert the amphoteric substance into a salt, and thus cause large errors in determination of physical constants. For this reason, the majority of physical constants are of practically no value for the characterisation of individual proteins. Other physical constants which have been determined are molecular weight, estimated chiefly by the measurement of the osmotic pressure of a solution contained in a membrane permeable to crystalloids and in contact with water or an aqueous solution, and electrolytic conductivity, of which measurements have been made in the course of investigations dealing with the salt formation of proteins. Much work remains to be done with reference to osmotic pressure, which probably varies with the state of aggregation of the protein. It is advisable to repeat here, that the coagulation temperature of proteins cannot be regarded as a physical constant (*see* above).

III. Classification of the Proteins.

Not sufficient is known yet of the true chemical structure of the proteins to found a rational classification based upon differences of chemical constitution. The classification adopted is therefore more or less of an empirical nature, founded only to a small extent on chemical distinctions, but chiefly on crude differences in physical properties. A classification was provisionally adopted by a joint committee of the Chemical and Physiological Societies, and subsequently submitted to American physiologists and chemists, who adopted a very similar but somewhat more complete classification. The appended classification includes the additions contained in the American list which were not contained in the English suggestions.

A. The Simple Proteins.

(*a*) *The protamines.* This class is a very limited one, the members of which are contained only in the testes of certain fish in conjunction with nucleic acid. These proteins are distinguished by their extremely basic character and high percentage of nitrogen (25–30 p.c.), and the large amount of diamino acids which they yield on hydrolysis (80 p.c. or more). They can be precipitated from basic solutions by phosphotungstic acid and other alkaloidal reagents.

(*b*) *The histones.* The members of this class are less basic than the protamines, but more basic than the following class of the albumins. There is no hard-and-fast distinction between the three classes. Like the protamines, the histones are also for the most part found in combination with nucleic acid as nucleoproteins, which form the nucleus of the cells. The histones contain 17–20 p.c. nitrogen, and yield on hydrolysis more diamino acids than albumins, but less than the protamines. They can be obtained from the nuclei of the blood-corpuscles of birds, from thymus glands, and from the ripe spermatozoa of various fish.

(*c*) *The albumins.* This is a very widely distributed class of proteins, the members of which are soluble in water, forming solutions which coagulate on heating. The animal albumins are not precipitated from neutral solutions by saturation with sodium chloride and magnesium sulphate and half saturation with ammonium sulphate. In this way they are distinguished from the globulins. The albumins derived from plants include generally those proteins which are soluble in water, as distinguished from those soluble in saline solutions only. The solutions of plant proteins also coagulate on heating, but, in distinction to animal albumins, some of them are precipitated from aqueous solution by half-saturation with ammonium sulphate. Both the animal and vegetable albumins are generally substances of amphoteric reaction, being both weakly acid and weakly basic. They contain, as a rule, about 16 p.c. nitrogen.

(*d*) *The globulins.* This class includes the proteins, which are generally insoluble in water, but soluble in saline solutions of moderate concentration. They are precipitated by saturation of their solutions with sodium chloride and magnesium sulphate, and by half-saturation with ammonium sulphate.

(*e*) *The prolamines.* The members of this class were formerly called the gliadins. They are the vegetable proteins, which are insoluble in absolute alcohol or water, but soluble in diluted alcohol (70 p.c.). Osborne designates them as prolamines, as they yield on hydrolysis a relatively large amount of proline and ammonia.

(*f*) *The glutelins.* These are the vegetable proteins, which are insoluble in dilute alcohol, water, and salt solutions. They can be dissolved by dilute acids and alkalis.

(*g*) *The scleroproteins.* The proteins of this class were formerly called the *albuminoids.* Included in this class is a miscellaneous collection of proteins of various character, such as horn, hair, silk, gelatin, &c. They are derived, as the name indicates, chiefly from the connective and supporting tissues, and have no common distinguishing properties, which can serve to characterise them as a class. Gelatin is soluble in water, but other members of the class are soluble in no solvents.

B. The Conjugated Proteins.

The proteins of this class are found to contain groups which were formerly designated 'prosthetic groups,' which do not yield only amino acids on hydrolysis.

(*a*) *The nucleoproteins.* Proteins found in combination with nucleic acid. These are said to form the chief constituent of nuclei, and are widely distributed.

(*b*) *The glycoproteins,* or proteins found in combination with a carbohydrate group.

(*c*) *The hæmoglobins* or proteins found in combination with the chromatogenic substance hæmin. Hæmoglobins form the red pigment of blood of various animals. Certain pigments of the algae are thought to be allied, as well as pigments derived from the bloods of invertebrates.

(*d*) *The phosphoproteins.* These proteins readily yield phosphoric acid on gentle hydrolysis with alkali. Included in this class are caseinogen, the chief protein of milk, and vitellin from egg-yolk. It is not certain whether this class should be included amongst the conjugated proteins.

(*e*) *The lipoproteins.* Very little is known with certainty as to this class. It cannot be stated definitely whether the fatty substances which are often isolated with proteins are in chemical combination or only physically adsorbed.

C. The Derived Proteins.

The substances included under this heading are derived from proteins by hydrolysis either by enzymes or by gentle treatment with acid and alkalis. They still give some of the definite protein reactions.

(*a*) *The proteans or metaproteins.* This class includes those substances derived from natural proteins by gentle treatment with acids or alkalis at moderate temperatures (in the incubator). In the former case, 'acid albumins' are formed, which are precipitated from solution on neutralisation, giving a precipitate which redissolves on addition of excess of alkali; in the latter case 'alkali albumins' are formed, which are precipitated on neutralisation with acid, but dissolve on addition of excess. These represent, perhaps, the most complex of the hydrolysis degradation products of the proteins.

(*b*) *The coagulated proteins.* The phenomena of coagulation have been already discussed.

(*c*) *The proteoses.* These substances are derived from proteins by enzymatic digestion. The proteoses are still somewhat complex substances, and can be precipitated from solution by salts, for which purpose zinc sulphate and ammonium sulphate are generally employed. The proteoses give characteristic protein reactions, such as the biuret reaction, and are not coagulated on heating.

(*d*) *The peptones.* These are still simpler hydrolytic degradation products of proteins, and differ from the proteoses in that they are not precipitated from solutions by salts, even on saturation.

(*e*) *The peptides.* Under this designation are included still simpler hydrolytic degradation products of proteins than the peptones, substances, for example, which yield on hydrolysis two or three amino acids only. There is no hard-and-fast line of demarcation between this class and the classes containing the more complex substances, such as the peptones. The peptides are generally crystalline substances, whereas the peptones are not. Very few peptides have up to the present been isolated directly by hydrolysis of proteins (*see* E. Fischer and Abderhalden, Ber. 1906, 39, 752, 2315; 1907, 40, 3544; Osborne and Clapp, Amer. Journ. Physiol. 1907, 18, 123). A large number of peptides have, however, been obtained synthetically by E. Fischer and his pupils. The preparation of these products may be regarded as the first stage in protein synthesis.

In the appended table is given a list of the chief naturally occurring proteins, with their origin and the class to which they are assigned. By reference to the description of the various classes given above, a conception can in most cases be formed as to the method of isolation. Thus the albumens can be extracted from natural products by water, the globulins by not too concentrated salt solutions, the prolamines by alcohol, &c. Some of the proteins are insoluble in solvents, such as horn, silk, and other scleroproteins. These can be prepared by separating the other constituents of the raw products by extraction with water, acids, ether, &c., when they alone will remain undissolved:—

The Chief Natural Proteins.[1]

Vegetable Proteins.

Name	Origin	Class
Abrin	Abrus seeds	Albumin
Amandin	Almonds	Globulin
Avenalin	Oats	„
Castanin	Chestnuts	„
Conglutins	Different lupins	„
Corylin	Hazel-nuts	„
Edestin	Hemp-seed	„
Excelsin	Brazil-nuts	„
Globulin	Squash-seeds	„
„	Cotton seeds	„
Gliadin	Wheat	Prolamine
Glutelin	„	Glutelin
Glycinin	Soya-bean	Globulin
Hordein	Barley	Prolamine
Juglasin	Walnut	Globulin
Legumelin	Lentil, horse-bean, vetch, etc.	Albumin.
Legumin	„ „ „	Globulin, precipitated by $\frac{6}{10}$ saturation with ammonium sulphate.
Leucosine	Wheat	Albumin
Maysin	Maize	Globulin
Oryzenin	Rice seeds	Glutelin
Phaseolin	Kidney-bean	Globulin

[1] See, however, next paragraph.

Name	Origin	Class
Phycocyan,[1] Phycoerythrin	Ceramium rubrum	Chromoproteins
Ricin	Castor bean	Albumin
Tuberin	Potato tuber	Globulin
Vicillin	Lentil, horse-bean, vetch, etc.	Globulin, precipitated by $\frac{7}{10}$ saturation with ammonium sulphate.
Vignin	Cow-pea	Globulin
Zein	Maize	Prolamine

Animal Proteins.

Name	Origin	Class
Albumin of egg (ovalbumin)	Eggs	Albumin
Albumin of milk (lactalbumin)	Milk	,,
Albumin of serum	Serum	,,
Bence-Jones protein	Certain pathological urines	Globulin (?)
Caseinogen	Milk	Phosphoprotein
Chondroproteins	Cartilage, tendons, etc.	Glycoproteins
Clupeine	Testes of herring	Protamine
Collagen	Connective tissue	Scleroprotein
Conalbumin (?)	Eggs	Albumin
Conchiolin	Shell of lamellibranchs	Scleroprotein
Cornein	Coral	Scleroprotein
α- and β-Crystallins	Lens of eye	Globulins
Cyclopterine	Testes of cyclops	Protamine
Elastin	Ligamentum nucæ	Scleroprotein
Fibrinogen. Yields fibrin on clotting	Blood	Globulin.
Gadus histone	Testes of Gadus	Histone
Gelatin	Closely allied to collagen	Scleroprotein
Globin	Separated from chromo-protein of blood.	Histone (?)
Globulin of egg (ovoglobulin)	Eggs	Globulin
,, milk (lacto-globulin)	Milk	,,
,, serum	Serum	,,
Gorgonin	Skeletal tissue, Gorgonia cavollini	Scleroprotein.
Hæmoglobin	Blood	Conjugated protein
Histone of thymus	Thymus gland	Histone
Keratins (various)	Hair, horn, nails, etc.	Scleroproteins
Lota histone	Testes of Lota	Histone
Myosin (para myosinogen)	Striated muscular tissue	Globulin
Myogen (myosinogen)	,, ,, ,,	Albumin
Mucins and mucoids	Various secreting glands (Animal mucilagenous substances generally)	Glycoproteins
Nucleoproteins	Animal and vegetable cells (supposed constituent of nucleus)	Nucleoproteins
Onuphin	Onuphis tubicola (worm)	Scleroprotein
Reticulin	Mucosa, small intestine of pig, etc.	,,
Salmine	Testes of salmon	Protamine
Scombrine	Testes of mackerel	,,
Silk gelatin	Silk	Scleroprotein
Silk fibroin	Silk	,,
Spongin	Sponges	,,
Sturine	Testes of sturgeon	Protamine
Thyreoglobulin	Thyroid gland	Globulin
Vitellin	Yolk of eggs	Phosphoprotein

IV. THE SEPARATION AND IDENTIFICATION OF THE NATURAL PROTEINS.

One of the chief difficulties encountered in the investigation of the proteins is that due to their separation from one another. So great has this been that in very many of the cases it is impossible to state whether a substance described under a given name is a chemical entity or a mixture. In the case of insoluble substances, such as the keratins, this statement can be readily understood. But even in the case of the soluble proteins, no satisfactory method for complete separation exists. This is due to the colloidal nature of the substances, so that if one substance is separated from solution, it will carry down with it, in state of adsorption, other substances, which in its absence would remain in solution. For these reasons, and in particular that the identification of an individual protein is not altogether easy, the list of proteins given above must be regarded as tentative only. It includes, however, most of the proteins which have been described under various names.

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[1] Kylin, Zeitsch. physiol. Chem. 1910, 69, 169.

Separation of Proteins from one another.—A few proteins, especially some of vegetable origin, can be separated by taking advantage of the fact that they are soluble in dilute alcohol. Others are soluble only in saline solution, and many of the vegetable proteins, furthermore, can be recrystallised from such solutions. Even in this case, as Osborne has shown, the product obtained is not pure, but is a mixture of the protein and its salt. The usual method for separating from one another proteins which are soluble in water is that of fractional precipitation by salts. For every protein in a given concentration there is a particular degree of saturation for each precipitating salt, at which the protein commences to separate from solution, and a certain degree of saturation at which the precipitation is complete. This method, which has been already discussed (*see* p. 406), is, however, very imperfect, and it is probably impossible in most cases to obtain a complete separation of two soluble proteins. A crude separation of such substances as globulins from albumins can, however, be accomplished (*cf.* Wiener, Zeitsch. physiol. Chem. 1911, 74, 29).

The Identification of Proteins.—The chief characteristic of individual proteins is the number and quantity of the various amino acids which are yielded on hydrolysis. A quantitative hydrolysis experiment is, however, only possible when relatively large amounts of material are available, and is an operation requiring a long time for its performance. It is therefore necessary in most cases to find some physical and chemical constants which may serve for identification.

A. *Physical constants.* Such well-defined constants as boiling-point, melting-point, which are used for identifying simpler substances, are not found in the case of the proteins. The temperature of heat coagulation (p. 404) has been already discussed, and as mentioned above, cannot be regarded as a reliable constant. Neither can the optical rotation, although most proteins are optically active. This is due to the large molecular weight of the proteins, and also their amphoteric character, which allows them to form salts in most cases with acids or bases in solution. A small quantity of an acid or base can therefore convert a relatively large amount of protein into salt, and thus considerably alter the physical properties of its solution. As, furthermore, it is difficult to free entirely protein solutions from electrolytes, even after prolonged dialysis, it may be readily understood that few determinations of physical constants of proteins are reliable. The most reliable, perhaps, as it is to a great extent independent of the factors just mentioned, is the precipitability by salts, and as has been suggested, the capacity for protecting colloidal gold from precipitation ('gold number') (*see* p. 406). On the whole the chemical methods are the more trustworthy for identification.

B. *Chemical constants.* The differences between the empirical compositions of the proteins are in the majority of cases small as regards the nitrogen, carbon, and hydrogen. In a few cases of the very basic proteins (the protamines) the total nitrogen is high. The chief difference is, however, in the sulphur constant, which is very readily determined by ordinary analytical methods. This factor gives a measure of the cystine in the molecule, and varies from 0 in certain proteins to 5 p.c. in human hair. The nucleoproteins contain phosphorus in the prosthetic group as nucleic acid, and the phosphoproteins yield phosphoric acid on hydrolysis at 37° with 1 p.c. sodium hydroxide. A few proteins contain halogens; the chief of these is the protein of the thyroid gland which contains iodine; this element is also contained in gorgonin, and iodine and bromine have also been isolated from several other scleroproteins derived from the supporting system of marine animals.

Another series of chemical constants which can be readily determined with small quantities of materials are the nitrogen distribution numbers, which are sometimes called the 'Haussmann numbers.' It will be remembered that the relative amounts of mono- amino and diamino acids vary very largely in the different proteins. The diamino acids are precipitated from the hydrolysis mixture by phosphotungstic acid. Proteins, furthermore, yield on hydrolysis small quantities of ammonia, which is supposed to be derived from nitrogen combined as 'amide,' and which can be readily estimated by making the hydrolysis mixture slightly alkaline (with magnesium hydroxide) and distilling off *in vacuô.* The distribution, therefore, of the total nitrogen of the protein between the 'amide' nitrogen, which can be distilled off as ammonia, the 'diamino acid' nitrogen, which is precipitated by phosphotungstic acid, and the 'mono-amino acid' nitrogen, which remains in the filtrate from this precipitate, is the chemical constant of proteins which is most readily determined and is most characteristic.[1]

Other chemical constants have also been suggested, as, for example, the tyrosine factor, or the amount of tyrosine which a given protein yields on tryptic digestion, and which is estimated by titration with potassium bromate solution, whereby the bromo-tyrosine is formed. Histidine probably also reacts with bromate, and the method has not been found so far to be entirely satisfactory. The acid and basic properties of the proteins also vary considerably. Except, however, in the case of such strongly basic substances as the protamines, and such strongly acid substances as caseinogen, the acid and basic functions can only be determined with difficulty, and for this purpose physical methods must be generally employed (*v.* van Slyke's method for estimating the hexone bases produced by hydrolysis).

C. *Biological reactions.* If a protein be repeatedly injected into an animal (rabbits are generally employed), the serum of that animal acquires the property of precipitating that protein (antigen). This reaction is known as the 'precipitin' reaction. The precipitin yielding serum will give the reaction only with the protein which produced it, or proteins

[1] See, however, footnote, p. 403.

closely allied. The reaction is characteristic rather of the species of the animal from which the antigen is derived than of its actual chemical characteristics. Thus a precipitin-yielding serum obtained by the injection of human blood into rabbits will give a precipitation with any of the proteins derived from the human body, and if the rabbit had been properly 'immunised' with a sufficient number of injections it will precipitate these proteins in very dilute solutions. Proteins derived from a species zoologically allied to a man, such as anthropoid apes, it will precipitate, but only in more concentrated solutions than are necessary to produce a precipitate in the case of proteins of human origin. This 'precipitin' reaction has been employed practically in meat inspection to determine the origin of the meat in sausages and other meat-containing material, when the origin cannot be ascertained by direct inspection. As to the chemical or physical nature of the precipitin reaction little is known.

V. The Conjugated Proteins.

(*a*) The Nucleoproteins.

This important class of proteins is found in most tissues, the nucleoproteins being generally assumed to be the chief constituent of the cell nucleus. They were first systematically investigated by Miescher, who showed that the spermatozoa of salmon and various other fish were composed chiefly of compounds of the strongly basic protamines, with an amorphous acid called nucleic acid. Nucleic acid is the essential non-protein group in this class of conjugated proteins, and is found in combination with other proteins than the strongly basic protamines. The nucleo-proteins can be extracted from tissues, &c., by dilute salt solutions or very dilute alkali. From the solution thus obtained they can be precipitated by dilute acetic acid. It is sometimes advisable to dry the tissues before extracting by treating with gradually increasing concentrations of alcohol, and finally with absolute alcohol and ether. On digesting nucleoproteins with enzymes, the protein part of the molecule is partially hydrolysed and a residue, soluble in alkalis, but insoluble in dilute acetic acid, is obtained, which is termed a nuclein.

Nucleic acid. It is important in this article to give a short account of this acid, which, although not a protein, is found only in combination with proteins to form substances of great physiological importance. As to the number of nucleic acids and the identity of the nucleic acids from various sources, nothing quite definite can be stated at the present time, although Steudel affirms that the nucleic acid obtained from such different sources as fish-spermatozoa and thymus gland of calf are identical.

Nucleic acid was originally obtained by Miescher by treating the nucleoprotein from fish spermatozoa with sodium hydroxide solution and throwing the solution of sodium nucleate thus obtained into an ice-cold solution of hydrochloric acid in alcohol. The operations must be carried out rapidly, as the nucleic acid is readily decomposed by mineral acids. The acid is, however, more stable in the presence of alkalis, and is now generally prepared directly from tissues, &c., without previously isolating the nucleoprotein. Thymus gland gives the largest yield. The gland is boiled with alkali, the hydrolysis mixture, after solution of the proteins, neutralised with acetic acid, and the filtrate from the precipitate thus obtained, thrown into alcohol, whereby sodium nucleate is precipitated; this is purified by solution in water and reprecipitation by alcohol. The free acid can be obtained from the sodium salt by alcoholic hydrochloric acid. Nucleic acid is a strong acid, which gives soluble alkali salts from solutions of which the free acid can be precipitated by mineral acids, but not by acetic acid. A 5 p.c. solution of sodium nucleate forms a gel. On hydrolysis with acids it yields the following groups of substances: (*a*) alloxuric bases (guanine, adenine, xanthine, and hypoxanthine; (*b*) pyrimidine bases, cytosine, uracil, and thymine; (*c*) carbohydrate derivatives, formic and lævulic acids, decomposition products of hexose; (*d*) phosphoric acid and ammonia. Of these products, xanthine, according to Steudel, is a secondary decomposition product produced by the action of acids on guanine, with scission of ammonia, and hypoxanthine and uracil are in a similar way produced from adenine and cytosine respectively. Steudel represents the hydrolysis of nucleic acid as follows:

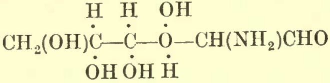
$$C_{43}H_{57}N_{15}O_{30}P_4+8H_2O+2O=\underset{\text{(Guanine)}}{C_5H_5N_5O}+\underset{\text{(Adenine)}}{C_5H_5N_5}$$
$$+\underset{\text{(Thymine)}}{C_5H_6N_2O_2}+\underset{\text{(Cytosine)}}{C_4H_5N_3O}+4\underset{\text{(Hexose).}}{C_6H_{12}O_6}+4HPO_3$$

According to this scheme, nucleic acid is a tetra-metaphosphoric acid, containing for each atom of phosphorus a hexose group (compare the glycerophosphates) and one molecule of a base. Recent researches of Levene and his pupils indicate that the ordinary nucleic acid is formed by the coupling up of single groups, termed nucleotides, each of which consists of a phosphoric acid residue combined with a carbohydrate and a base. The nucleic acid of thymus would be formed from four such groups, each containing a different base. The nucleotides themselves can be broken down, according to the method of hydrolysis, into complexes containing phosphoric acid and a carbohydrate, or into complexes containing carbohydrate and base (Ber. 1908, 41, 1905, 2703; 1909, 42, 335, 1198, 2474, 2469, 2703).

Nucleic acids from yeast, wheat embryos, and other sources have also been investigated. Certain other allied substances, such as guanylic acid (from pancreas) and inosinic acid (from meat extract) have been described, which yield on hydrolysis pentoses instead of hexoses. These are possibly nucleotides (*see* papers of Levene already quoted above).

b. The Glycoproteins.

In this group is included a large number of mucilagenous substances, which are widely distributed in the animal kingdom. Included amongst them are the mucins of egg-white serum, salivary glands, ascitic fluids, &c. They are, for the most part, precipitated from solutions by very weak alkali. Properly speaking, they should not perhaps be classed as conjugated proteins, as they yield on vigorous hydrolysis the amino-sugar glucosamine—



$$\mathrm{CH_2(OH)\overset{H}{\underset{OH}{\dot{C}}}—\overset{H}{\underset{OH}{\dot{C}}}—\overset{OH}{\underset{H}{\dot{O}}}—CH(NH_2)CHO}$$

This is a reducing substance, and is probably combined in the molecule in a similar way to that in which the amino acids are combined, and cannot be separated from the conjugated amino acid groups by gentle treatment in the same manner, for example, as globin can be separated from hæmo-globin. It has been already stated that many crude proteins give reactions characteristic of a carbohydrate group (*see Protein reactions*). This is due to the fact that the crude proteins are often contaminated with these mucin-like glycoproteins.

In addition to these, another class of substance is also included amongst the glycoproteins, which are derived chiefly from cartilage and tendons. These contain the group chondroitin sulphuric acid. The constitution of this substance is not known, and very few additions to the knowledge of the chemistry of the cartilage substances has been made since Schmiedeberg's classical paper on the subject (Archiv. f. exp. Path. Pharm. 1891, 28, 355).

The chemistry of all substances included amongst the glycoproteins may be stated to be still in a very elementary condition.

c. **The Hæmoglobins.**

These contain the prosthetic group hæmin, which can be separated in the form of the hydrochloride hæmatin from the protein globin by very dilute acid. The hæmins are apparently closely allied to other natural pigments, especially chlorophyll.

VI. The Derived Proteins, and the Hydrolysis of Proteins by Enzymes.

Whilst hydrolysis with strong hot acid solutions leads to the degradation of proteins into simple amino acids, hydrolysis with more dilute acids or alkalis at lower temperatures leads to the formation of products in which two or more amino acids remain conjugated together, forming, according to the degree of complexity, peptides, peptones, proteoses (formerly called albumoses), and proteans (acid and alkali albumens). These products can also be obtained by hydrolysis with proteoclastic enzymes, which are widely distributed both in the animal and vegetable kingdoms. The principal amongst the former are pepsin, from the glands of the stomach, which acts in acid solution; trypsin, from the pancreas, which acts in alkaline solution; and erepsin, from the small intestine, which acts best in nearly neutral solution. The different enzymes produce differing degrees of hydrolysis, each enzyme producing a complex mixture. In a few cases only has a homogeneous product formed from the conjugation of two or more amino acids been isolated from the digestion products. The hydrolytic action of pepsin is the least of the proteoclastic enzymes of the digestive tract; trypsin has a stronger hydrolytic power, whereas erepsin can convert the already relatively simple peptones into simple amino acids. The separation of the enzymatic hydrolysis products into separate fractions is a purely arbitrary one, depending on the precipitation by salts of various concentrations. Thus, for example, Witte's peptones, a commercial product, obtained by the action of pepsin on fibrin, has been separated into the following fractions by zinc sulphate: from (2 p.c. solution): Fraction I., precipitation commences with 30 p.c. saturation, and is complete at 46 p.c.; Fraction II., precipitate between 58 and 64 p.c. saturation; Fraction III., precipitated between 72 and 82 p.c. saturation; Fraction IV., precipitated between 86 and 100 p.c. saturation. In addition to these, the product also contains fractions which are not precipitated by salts, and simple amino acids. As already stated, separation by salt fractionation is a very incomplete process. Various names have been given to such fractions (primary albumose, secondary albumoses A, B, and C). Similar arbitrary separations by graded strength of alcohol have also been effected. The more complex the hydrolysis products, the more readily are they precipitated by salt solutions; but little progress can be expected in the isolation of the complex intermediary hydrolysis products, which still possess the distinct characteristics of proteins, until new methods for the separation of colloids have been discovered.

Other methods for following the course of protein degradation by enzymes have been employed, amongst which may be mentioned the measurements of changes of viscosity and electrical conductivity of the hydrolysis mixtures, and above all Sörensen's titration method. When an amino acid is treated with formaldehyde, the latter, according to Schiff, acts on the amino group to form a methyleneimino derivative. This is a fairly strong acid, owing to the elimination of the amino group, and can be titrated with alkalis in the presence of phenolphthalein. As hydrolysis of the protein proceeds, scission of amino acids takes place according to the scheme—

$$\mathrm{-CH-NH-CO-+H_2O=-CH{\cdot}NH_2+COOH-}$$

The hydrolysis products increase in acidity after treatment with formaldehyde. In this way the relative number of amino groups set free by hydrolysis can be determined. Also, with increasing hydrolysis, the viscosity and electrical conductivity of the mixture alter.

The enzymes have a special predilection for certain groups; thus, for example, the tryptic enzyme causes a rapid scission of the tryptophan group. This specific action depends, furthermore, not only on the chemical structure of the group, but also on the stereo-chemical configuration of the group and of the whole molecule. The action of various proteoclastic enzymes on the synthetic polypeptides has formed the subject of exhaustive study by Abderhalden and his pupils, which are described in numerous papers (Zeitsch. physiol. Chem.).

Other derivatives of proteins have been described which are obtained by the action of chemical reagents. Thus the halogens, especially chlorine and bromine, readily react with the proteins. Nitrous acid also reacts. It is difficult to say, however, whether the various substances thus obtained are chemical entities.

Although general protein chemistry may be still considered in its infancy, the literature of the subject is already extensive. Various aspects have, however, been summarised in a large number of recent monographs, to which the reader is referred for more detailed information.

Bibliography.—Abderhalden: Biochemische Arbeitsmethoden, Berlin, 1910. Numerous articles on the methods of preparation and general chemistry of simple and conjugated proteins.

Oppenheimer: Handbuch der Biochemie, Jena, 1908. Also contains articles by various authors.

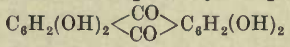
Aders Plimmer and Hopkins (edited by), Monographs on Biochemistry, 1908, R. H. Aders Plimmer, Chemical Constitution of the Proteins (two parts); Osborne, The Vegetable Proteins; Schryver, The General Characters of the Proteins.

Emil Fischer's collected papers (Untersuchungen über Aminosäuren, &c., Berlin, 1910) deal chiefly with the isolation and synthesis of amino acids and the synthesis of the peptides.

S. S.

PROTOCATECHUIC ACID. Six dihydroxybenzoic acids are possible theoretically, and all are known. Of these protocatechuic acid is the most important.

Protocatechuic acid, 3 : 4-*Dihydroxybenzoic acid.* This acid is of interest from the number of vegetable principles from which it may be obtained and which may therefore be regarded as containing the same grouping of the substituted radicles in the benzene nucleus. It is formed by fusing with potash oil of cloves, vanillin, piperic, caffeic, ferulic, hemipinic, and other acids, apiin (a substance present in parsley), quercetrin, kalotannin, Quebracho Colorado gum, and a large number of natural resins (Barth, Annalen, 154, 364; 159, 232; Hlasiwetz and Barth, *ibid.* 130, 346; 134, 277; 139, 78; Hlasiwetz and Grabowski, *ibid.* 139, 96; Hlasiwetz and Pfandler, *ibid.* 127, 357; Hesse, *ibid.* 112, 52; 122, 221; Fittig and Macalpine, *ibid.* 168, 111; Fittig and Remsen, *ibid.* 159, 129; Strecker, *ibid.* 118, 311; Offermann, *ibid.* 280, 24; Beckett and Wright, J., 1876, 808; Kraut and Dellder, Annalen, 128, 285; Malein, *ibid.* 134, 118; Perkin, Chem. Soc. Trans. 1897, 811; 1900, 424; Knox and Prescott, J. Amer. Chem. Soc. 1898, 20, 34; Arata, Chem. Soc. Abstr. 1878, 986). It is also formed by treating quinic acid with the mould *Micrococcus chinicus* (Löw, Ber. 1881, 453; Emmerling and Abderhalden, Centr. Bakt. Par. 1903, 10, 337). Protocatechuic acid may be prepared by gradually adding East Indian kino as a fine powder to 3 parts of fused potash. When the mass becomes light orange in colour, it is poured on to a cold plate to cool, then broken up and dissolved in hot water containing a little dilute sulphuric acid. After standing for 24 hours, sodium sulphate crystallises out. The liquid is filtered off and extracted with ether. The ether is evaporated off and the crude acid recrystallised from hot water (Stenhouse, Chem. Soc. Trans. 1875, 8). According to Hlasiwetz and Barth (Annalen, 130, 340), the acid is best purified by precipitating the lead salt with lead tartrate and subsequently decomposing the salt with sulphuretted hydrogen. It may also be prepared by heating 1 part of catechol, 4 parts of ammonium carbonate, and 5 parts of water in sealed tubes at 130°–140° (Miller, Chem. Soc. Trans. 1882, 399); by the action of potassium persulphate on *p*-hydroxybenzoic acid in alkaline solution (Chem. Farb. Schering. D. R. P. 81298; Frdl. iv. 121); by condensing chloracetic acid with eugenol and heating the product with caustic alkali at 230°–250° (Lederer. D. R. P. 80747; Frdl. iv. 151); by fusing *p*-chlor- or *p*-brom-*m*-hydroxybenzoic acid with caustic alkali at 180°–200° (Merck. D. R. PP. 71260, 74493; Frdl. iii. 849; Ber. Ref. 1894, 531). Protocatechuic acid crystallises in colourless prismatic needles, m.p. 199°. Readily soluble in boiling, less soluble in cold water: very soluble in alcohol, less soluble in ether. Crystallises from hot water with 1 molecule of water of crystallisation, which it loses on heating to 105°. Heat of solution of anhydrous acid, −5·82 cal. (Massol, Bull. Soc. chim. 1900, [iii.] 23, 231; Imbert, *ibid.* 832; Berthelot, Compt. rend. 101, 541). Decomposes on distillation or on heating with potash into carbon dioxide and pyrocatechol. Bromine in the cold reacts to yield bromoprotocatechuic acid (Barth, Annalen, 142, 246), but excess of bromine at 100° yields hydrogen bromide, carbon dioxide, and tetrabromopyrocatechol $C_6H_2Br_4O_2$ (Stenhouse, Chem. News. 29, 95; Chem. Soc. Trans. 1875, 7). Nitrous acid converts protocatechuic acid into oxalic and carboxytartronic acids ($C_4H_6O_8$), small quantities of picric acid, 2:4-dinitrophenol, 3 nitro-*p*-hydroxybenzoic acid, and dinitrohydroxyquinone (Grube, Ber. 12, 514). By eletrolytic oxidation in dilute sulphuric acid solution catellagic acid is formed (A. G. and F. M. Perkin, Chem. Soc. Trans. 1908, 1196). By heating protocatechuic acid with 2 parts of benzoic acid and 50 of sulphuric acid (66°B.) at 140°, a deep brown substance is obtained, producing with mordants almost the same shades as with alizarin; it is probably rufiopine



$$C_6H_2(OH)_2\!<\!\begin{smallmatrix}CO\\CO\end{smallmatrix}\!>\!C_6H_2(OH)_2$$

(Noelting and Bourchart, Bull. Soc. chim. [ii.] 37, 394). By heating it with pyrocatechol or resorcinol and zinc chloride at 150°, isomeric tetrahydroxydiphenylketones are obtained, which can be used to dye and print chrome mordanted cotton (Farb. Meister, Lucius, and Brüning, Eng. Pat. 19847; J. Soc. Chem. Ind. 1892, 902).

Protocatechuic acid gives with ferric chloride an intense bluish-green colouration, which on addition of sodium carbonate changes to deep red (*v.* also PYROCATECHOL) (Lutz, Chem. Zeit. 31, 570).

α-Resorcylic acid, 3 : 5-*Dihydroxybenzoic acid.* Prepared by fusing 1 : 3 : 5-disulphobenzoic acid with potash (Barth and Senhofer, Annalen, 159, 222; Hopfgartner, Monatsh. 14, 685); m.p. 232°–233° (B. and S.), 225°–227° (H.); sparingly soluble in cold water, very soluble in hot water, alcohol, or ether; gives no colouration with ferric chloride. On warming α-resorcylic acid with 4 parts of sulphuric acid at 140°, it dissolves with a deep red colour, addition of water changes the colour to green, flocks of anthrachrysone $C_{14}H_8O_6$ being formed, and if it is heated with benzoic acid in addition to sulphuric acid, xanthopurpurin $C_{14}H_8O$ is also formed. Oxidation with persulphate in concentrated sulphuric acid gives a yellow dyestuff (Bad. Anil. und Soda Fab. D. R. P. 85390; Frdl. iv. 360). Azo dyestuffs with amino-carboxylic acids *v.* Bayer and Co. D. R. P. 60500; Frdl. iii. 620; blue oxazine dyestuffs with nitrosodialkylanilines *v.* Bad. Anil. und Soda Fab. D. R. P. 57938; Frdl. iii. 370.

Pyrocatechol-*o*-carboxylic acid 2 : 3-*Dihydroxybenzoic acid.* Prepared by fusing 3-iodosalicylic acid with potash (Miller, Annalen 220, 126) or in small quantities, together with protocatechuic acid, by heating catechol, ammonium carbonate and water at 140° (Miller, *ibid.* 116), m.p. 204°.

3-*methyl ether* (*guaiacolcarboxylic acid*). Prepared by the action of carbon dioxide on the hot alkali salts of guaiacol (Heyden. Nachf., D. R. P. 51381; Frdl. ii. 132); m.p. 152° (Fritsch, Annalen, 301, 354).

β-Resorcylic acid, 2 : 4-*Dihydroxybenzoic acid.* Prepared by fusing *p*-cresolsulphonic acid with potash (Ascher, Annalen, 161, 11); by heating resorcinol with ammonium carbonate and water at 120°–130° (Brunner and Senhofer Ber. 1880, 2356); by fusing β-resorcylaldehyde or umbelliferone with potash (Tiemann and Reimer, Ber. 1879, 997; Tiemann and Parrisius, *ibid.* 1880, 2358); by heating 20 grms. resorcinol with 100 grms. potassium bicarbonate and 200 grms. water for 1½ hours on the water-bath, saturating with hydrogen chloride and extracting with ether. The ethereal solution is shaken with sodium hydoxide, the aqueous layer drawn off, acidified, and re-extracted with ether (Bistrzycki and Kostanecki, Ber. 1885, 1985). M.p. (anhydrous) 213°; readily soluble in warm water, alcohol, or ether; aqueous solution is coloured violet on addition of a little calcium chloride solution, the colour changing to yellow-brown on addition of more calcium chloride. For methylation *v.* Gregor, Monatsh. 16, 882.

Gentisic acid, *Hydroquinonecarboxylic acid, Quinolcarboxylic acid,* 2 : 5-*Dihydroxybenzoic acid.* Prepared by fusing 5-iodosalicylic acid with potash (Lautemann, Annalen, 12, 311; Liechti, *ibid.* Suppl. 7, 144; Demoli, Ber. 1874, 1438; Goldberg, J. pr. Chem. [ii.] 19, 371; Miller, Annalen, 220, 124), and similarly from the bromo compound (Rakowski and Leppert, Ber. 1875, 789); by the action of nitrous acid on 5-aminosalicylic acid (Goldberg, *l.c.*); by fusing gentisin with potash (Hlasiwetz and Habermann, Annalen, 175, 66); by heating hydroquinone, potassium bicarbonate and 4 parts of water to 130° and subsequently treating it with potassium sulphite (Senhofer and Sarlay, Monatsh. 2, 448); by treating *p*-dihydroxyphthalimide with strong hydrochloric acid (Thieler and Meisenheimer, Ber. 1900, 676); and by oxidising salicylic acid with potassium persulphate in alkaline solution (Chem. Fabr. Schering. D. R. P. 81297; Frdl. iv. 127), m.p. 200°; readily soluble in water, alcohol, or ether; insoluble in chloroform and benzene (Tiemann and Müller, Ber. 1881, 1988). Dry distillation yields carbon dioxide and hydroquinone. Ferric chloride gives a deep blue colour; when heated, gentisic acid reduces Fehling's solution. Oxidation with manganese dioxide and sulphuric acid, *v.* Juch, Monatsh. 1905, 26, 839. Bromo derivatives, *v.* Hemmelmayr, Monatsh. 1909, 30, 255.

5-*methylether* is prepared by treating the acid with 2 mols. of potassium hydroxide and 2 mols. of methyl iodide (Kostanecki and Tambor, *ibid.* 16, 920); m.p. 141°–142°.

2 : 6-Dihydroxybenzoic acid. Formed together with 2 : 4-dihydroxybenzoic acid by heating resorcinol with 4 parts ammonium carbonate and 5 parts water at 120°–130° (Senhofer and Brunner, Ber. 1880, 2356); decomposes without melting at 148°–167° into carbon dioxide and resorcinol. On adding a small quantity of ferric chloride a violet colour is produced, changing to blue with a further quantity of the reagent.

PROTOSAL *v.* SYNTHETIC DRUGS.

PROUSTITE, or light red-silver ore (Ger. *Lichtes Rothgiltigerz:* Span. *Rosicler claro*). Silver sulpharsenite Ag_3AsS_3 crystallised in the rhombohedral system. It forms transparent scarlet crystals with a brilliant adamantine lustre, which soon blacken on exposure to sunlight. The scarlet streak serves to distinguish proustite from the closely allied mineral pyrargyrite (*q.v.*). Hardness 2½; sp.gr. 5·57. It occurs in metalliferous veins, and at Chañarcillo in Chile, and is of importance as an ore of silver (Ag 65·4 p.c.). Named after the French chemist J. L. Proust (1754–1826), who distinguished it from pyrargyrite. L. J. S.

PRULAURASIN *v.* GLUCOSIDES.

PRUNETIN. The bark of the *Prunus serotina* (Ehrh.) contains a glucoside *prunitrin* $C_{22}H_{24}O_{11},4H_2O$, fine needles, which when hydrolysed with boiling dilute hydrochloric acid yields prunetin and glucose.

Prunetin $C_{15}H_9O_4{\cdot}OCH_3$, colourless needles, m.p. 242, dissolves in alkalis with a slight yellow colour, and is sparingly soluble in all the usual solvents. *Monacetylprunetin* $C_{16}H_{11}O_5(C_2H_3O)$, pale yellow needles, m.p. 190; *diacetylprunetin* $C_{16}H_{10}O_5(C_2H_3O)_2$, m.p. 224°–226°; *benzoylprunetin* $C_{16}H_{10}O_5(C_7H_5O)_2$, needles, m.p. 215°; *methylprunetin* $C_{15}H_8O_3(OCH_3)_2$, needles m.p. 145°; and *acetylmethyl prunetin*

$$C_{15}H_7O_3(OCH_3)_2C_2H_3O$$

have been prepared.

Fused with caustic potash at 250°, prunetin gives *phloroglucinol* and p-*hydroxyphenylacetic acid.*

Prunetol $C_{15}H_{10}O_5$, colourless needles, m.p. 290°, is formed by the demethylation of prunetin with hydriodic acid, and yields *acetylprunetol* $C_{15}H_7O_5(C_2H_3O)_3$, and *prunetol sulphate*

$$C_{15}H_{10}O_5{\cdot}H_2SO_4$$

yellow needles. On methylation with methyl iodide *prunetol dimethyl ether* identical with prunetin monomethyl ether, and a sparingly soluble methyl ether, the acetyl derivative of which melts at about 186°, are produced (Finnemore, Chem. Soc. Trans. 1910, 98, 1102).

A. G. P.

PRUNISIN *v.* GLUCOSIDES.

PRUSSIAN BLUE *v.* CYANIDES.

PRUSSIAN BROWN *v.* PIGMENTS.

PRUSSIAN RED or **VENETIAN RED** *v.* PIGMENTS.

PRUSSIATE OF POTASH *v.* CYANIDES.

PRUSSIC ACID *v.* CYANIDES.

PSEUDOCAPROIC ACID *v.* CAPROIC ACIDS.

PSEUDOCUMENE *v.* CUMENES.

PSEUDOCUMENOL *v.* PHENOL AND ITS HOMOLOGUES.

PSILOMELANE. An abundant ore of manganese, readily distinguished from the other black oxides of manganese (pyrolusite, manganite, and wad) by its greater hardness (H.$=5\frac{1}{2}$) and its characteristic mamillated, botryoidal, and stalactitic forms. It is variable and complex in composition, containing MnO_2 70–83, MnO 3–8, H_2O 3–6 p.c., together with smaller but widely varying amounts of barium (BaO up to 16 p.c.), potassium (K_2O to 6 p.c.), &c. Sp.gr. 3·7–4·7. Adopting the suggestion of Laspeyres (1876) of the hypothetical acid H_4MnO_5, L. L. Fermor (Mem. Geol. Survey, India, 1909, xxxvii.) regards the mineral as a manganate with the general formula—

$$mR_2''MnO_5+nR_4'''(MnO_5)_3$$

where R''=Mn, Ba, K_2, H_2, (Fe, Ca, Mg, Na_2, Co, Ni, Cu, Zn), and R'''=Mn, Fe, (Al). Lacroix, on the other hand, places the mineral in his group of manganites and separates romanechite (from Romanèche, France) as a distinct species with the formula $H_2(Mn,Ba)Mn_3O_8$, that of ordinary psilomelane being given as

$$xRO{\cdot}yMnO_2{\cdot}zH_2O.$$

The name psilomelane (from ψιλός, naked, and μέλας, black) is descriptive of the smooth, black, and shining surfaces of the mineral, and the German name *Schwarzer Glaskopf* also refers to this characteristic appearance. The mineral has a brownish-black streak, and breaks with a smooth fracture, with sometimes indications of a fibrous crystalline structure. Fermor has separated distinctly crystallised varieties of the Indian mineral under the name hollandite (*q.v.*). Psilomelane has the same mode of occurrence as pyrolusite (*q.v.*), and the two minerals are mined together in large quantities. In India it is the most abundant of the manganese ores. L. J. S.

PSITTACINITE *v.* Vanadium.

PTERITANNIC ACID *v.* Filix mas.

PTOMAINES. The word 'ptomaine' was first introduced by Selmi to signify the poisonous products of putrefaction giving the reactions which had hitherto been looked upon as characteristic of the vegetable alkaloids. The term 'alkaloid' was applied to basic substances which gave precipitates with certain reagents, *e.g.* potassium mercury iodide, phosphotungstic acid, &c. (*see* art. Vegeto-alkaloids), and a ptomaine was a poisonous alkaloid derived from the action of bacteria on the animal tissues after death; many of the substances described under the name, however, are non-poisonous, and though basic would not be included under the present definition of alkaloid as 'a base which contains a cyclic nitrogenous nucleus.'

As early as 1856, Panum had found that a toxic substance which was not destroyed on boiling, and which was similar to curare in its physiological effects, was present in certain septic fluids. Dupré and Bence-Jones (Zeitsch. Chem. Pharm. 1866) described a substance extracted from the animal body which gave the reactions of an alkaloid, and a blue fluorescence in sulphuric acid solution, and which they called 'animal quinoidine.' About the same time, Marquardt described an alkaloidal substance 'septicine,' which he obtained from a corpse, and which gave reactions similar to those of coniine. Among other workers were Schmidt, and Bergmann and Schmiedeberg, who described a toxic crystalline substance 'sepsin,' which, when injected into the body, produced symptoms of septicæmia; Zuelzer and Sonnenschein (1869) who obtained a very small quantity of a substance resembling atropine in its physiological action; and Roersch and Fasbender (1871) who isolated a non-crystalline substance with properties similar to those of digitalin. Selmi, from 1873 onwards, obtained from putrefying corpses and from various proteins a number of substances similar in their physiological action to the vegetable alkaloids delphinine, morphine, muscarine and strychnine. Nencki (1876) isolated collidine from the putrefactive products of gelatin and prepared and analysed the platinichloride. Gautier and Etard prepared the same substance from putrid mackerel, together with another base of formula $C_9H_{13}N$, isomeric with parvoline. The chief worker on the subject was Brieger (Die Ptomaine, Parts I., II., III., 1885 and 1886), who elaborated methods of isolation and was successful in obtaining a large number of bases from putrefying horse and ox flesh, from various kinds of fish, and from corpses. Among these are included mono-, di-, and trimethylamines, diethylamine, choline, neurine, neuridine, gadinine, cadaverine and putrescine, saprin and muscarine. He also obtained typhotoxine from the flesh of a victim of typhus fever, and "tetanine" from the body of a man who had died of tetanus.

There is very little evidence that the so-called "ptomaine poisoning" is in general due to the presence of poisonous bases derived from the putrefaction of meat and other foods. Vaughan found in cheese which had produced pathological symptoms in those who had partaken of it, a poisonous substance which he separated in a crystalline condition and which when injected into the animal body produced the same symptoms as did the cheese from which it was derived. He called the substance tyrotoxicon, but made no analysis of it. Brieger isolated from poisonous mussels a ptomaine which he called mytilotoxine. In most of the cases of ptomaine poisoning, however, no chemical examination of the foods in question has been made, and the diagnosis has been based mainly on the symptoms or on the results of bacterial examination. The toxicity of extracts of foods which have caused epidemics of poisoning is generally removed by boiling (Durham, Brit. Med. J. 1898). Brieger isolated cadaverine and putrescine from pure cultures of pathogenic bacteria; these substances, however, are not poisonous.

Of the origin of ptomaines in the body very little is known. Lecithin seems to be looked upon as an intermediate substance between proteins and ptomaines, and neurine and choline have been obtained as decomposition products of lecithin. Brieger found that different ptomaines were obtained according to the length of time allowed for putrefaction. Thus corpses which had been allowed to putrefy for three days gave chiefly neuridine; after seven days methylamine, and after eleven days cadaverine were the chief products. It seems probable from these results that prolonged treatment brings about the conversion of one base into another.

Gautier separated from fresh tissues a

number of bases of the uric acid and creatinine groups, some of which have a marked toxic effect. To these substances which are present in the body as the result of ordinary metabolism, he gave the name *leucomaines*, to distinguish them from the substances formed by bacterial action. The chief of them are: carnine, adenine, guanine, xanthine, hypoxanthine, pseudoxanthine, creatinine, xanthocreatinine, crusocreatinine and amphicreatinine.

Method of isolation. The methods used by the earlier investigators were those by which the vegetable alkaloids were extracted, the chief of which is known as the Stas-Otto process (*see* art. VEGETO-ALKALOIDS). Brieger's method, however, seems to be the most satisfactory for the extraction of ptomaines. The putrefying flesh is minced as finely as possible and boiled with water. The aqueous extract is treated with lead acetate and filtered, and the filtrate is treated with hydrogen sulphide to precipitate the excess of lead. It is then evaporated and extracted with amyl alcohol. The extract after repeated washing with water is concentrated, made strongly acid with sulphuric acid and shaken with ether to remove oxyacids. The solution is then evaporated and volatile fatty acids are thus removed. The sulphuric acid is removed by baryta, and the excess of baryta precipitated by carbon dioxide. The ptomaines are then precipitated by addition of mercuric chloride with which they form compounds, the precipitate is decomposed by hydrogen sulphide, filtered, and the filtrate concentrated. Inorganic substances crystallise out first, and the ptomaines crystallise from the residual liquors or are left as syrups on evaporation. The separation of the ptomaines from one another is accomplished by fractional precipitation or crystallisation of the platinichlorides, aurichlorides, or mercurichlorides. Baumann and Udransky (Zeitsch. physiol. Chem. 13, 562) separated cadaverine and putrescine by the different solubilities of their benzoyl derivatives in alcohol and ether, and this method has been used by other workers.

Of the substances described as ptomaines by their discoverers, the methyl- ethyl- and propyl amines are described in special articles, as are also choline and the pyridine bases collidine, hydrocollidine, and others (*see* art. BONE OIL, vol. I.). The earlier known substances, animal quinoidine, septicine, sepsin, and various others described by later authorities, have not been obtained in a pure condition and their composition is unknown. Of the others the following are the most important.

Cadaverine $C_5H_{14}N_2$. *Pentamethylene diamine.* Non-poisonous. Isolated by Brieger, 1885. Found also in urine and in fæces in cases of cystinuria. Prepared synthetically by Ladenburg (Ber. 19, 2585) by treatment of an ethereal solution of trimethylene cyanide with zinc and hydrochloric acid. Syrup; b.p. 178·9. Easily soluble in water and alcohol; with difficulty in ether. Forms well defined hydrochloride, mercurichlorides, and platinichloride; also oxalates.

Gadinine $C_7H_{16}NO_2$. Non-poisonous. Obtained together with muscarine from putrefying cod (Brieger). Formula obtained from analysis of its platinichloride.

Muscarine $C_5H_{13}NO_2$. Poisonous. Discovered by Schmiedeberg and Koppe in toadstools, and by Brieger in putrefying fish. Has been prepared synthetically by action of monochloracetal on trimethylamine; also by oxidation of choline by nitric acid. Hence formula obtained is $CHO{\cdot}CH_2NMe_3OH$.

Neuridine $C_5H_{14}N_2$. Non-poisonous. Isomeric with cadaverine. Free base very unstable. Found in fresh tissues as well as in the products of putrefaction of fish, cheese, and gelatin. Hydrochloride, platinichlorides and aurichlorides crystallise well. Slightly soluble crystalline picrate known.

Neurine $C_5H_{13}NO$. Poisonous. *Trimethyl vinyl ammonium hydroxide.* Syrup. Gives well crystallised platinichloride, picrate, and mercurichloride.

Putrescine $C_4H_{12}N_2$. *Tetramethylene diamine.* Generally found with cadaverine in putrefying tissues. Prepared by the action of sodium on alcoholic ethylene cyanide. Crystalline; m.p. 27°–28°; b.p. 158°–160°. Gives well-defined aurate, platinichloride, and picrate.

Saprin $C_5H_{14}N_2$. Non-poisonous. Isomeric with cadaverine, from which it differs by the different solubility of its platinichloride.

Mytilotoxine $C_6H_{15}NO_2$. Found by Brieger and Salkowski (1887) in poisonous mussels. Formula found from analysis of its aurichloride.

Typhotoxine $C_7H_{17}NO_2$. Obtained from pure cultures of typhoid bacillus. Gives aurichloride which melts about 176°.

Tetanine $C_{13}H_{22}N_2O_4$. Strongly alkaline yellow syrup. Obtained from the flesh of a case of tetanus. Gives deliquescent platinichloride which decomposes at 197°. M. B. T.

PTYALIN *v.* DIASTASE.

PUCHERITE *v.* VANADIUM.

PULEGENONE, PULEGONE *v.* KETONES.

PULMOFORM *v.* SYNTHETIC DRUGS.

PUMICE, or **Pumice-stone.** A frothy form of volcanic glass, formed by the expansion of occluded water-vapour when the molten lava flowed out at the earth's surface. The glassy obsidian (*q.v.*), invariably associated with pumice, represents the same magma which had consolidated under a somewhat greater pressure. This is proved by the fact that fragments of obsidian when heated in a crucible to the point of fusion suddenly swell up, and are converted into pumice. An artificial pumice may be made by blowing steam or air through molten slag or glass. Volcanic lavas of various kinds may assume the pumiceous form, but it is only those richer in silica (corresponding with rhyolite and obsidian, *v.* LAVA) that yield a pumice of economic value. The following analyses are given by G. P. Merrill (The Non-Metallic Minerals, 2nd edit., 1910): I. of pumice from Capo di Costagna, Lipari Islands; II. of pumice-dust from Orleans, Harlan Co., Nebraska:—

	SiO_2	Al_2O_3	$\begin{cases} Fe_2O_3 \\ FeO \end{cases}$	CaO	MgO	K_2O	Na_2O	Loss on ignition.	Total.
I.	73·70	12·27	2·31	0·65	0·29	·73	4·25	1·22	99·42
II.	69·12	17·64		0·86	0·24	6·04	1·69	4·05	100·24

Owing to its cellular structure, pumice floats on water, but the sp.gr. of the powdered material is 2·3 to 2·4. The vesicules are either round or elongated (due to the flowing of the lava), and the glass has the form of thin partitions or threads. It is on this peculiarity of structure that the abrasive qualities of the material depend. The presence of minute crystals of felspar, &c., is detrimental, since, being harder, these produce scratches on the work. Blocks of pumice are used for cleaning and smoothing; but with coach-builders, &c., it is now, to a certain extent, replaced by an artificially prepared stone. Powdered pumice or pumice-dust is used in the manufacture of metal polishes and scouring soaps. This is often mistaken for diatomaceous earth or kieselguhr (*q.v.*), from which it may readily be distinguished under the microscope (pumice powder consisting of irregular, glassy fragments) and by chemical tests (kieselguhr being a hydrated silica soluble in caustic soda solution).

Pumice is found in several volcanic districts, but the chief commercial source for the better qualities of material is in the Lipari Islands north of Sicily. The best material is from Campo Bianco, Monte Pelato, and Monte Chirica on Lipari. On this island there are some 170 quarries and mines producing about 6000 tons of pumice per annum. The price varies from 30 to 3000 lire per ton, being usually 350 to 500 lire for assorted material. An inferior grade, called 'alessandrina,' is used in brick-shaped pieces for smoothing oilcloth. Small quantities of pumice are also exported from Teneriffe. In the United States enormous beds of pure white pumice-dust are found over wide areas in Nebraska, Kansas, California, Idaho, Utah, South Dakota, Wyoming, Oregon, Colorado, Oklahoma, and Iowa. The annual production amounts to about 10,000 tons, and comes chiefly from Harlan and Lincoln counties, Nebraska. This material is of the nature of a volcanic ash or dust, the lava having been blown into fine fragments by the expanding water-vapour and scattered by the winds. It is largely used for polishing powders and soaps; other suggested applications are for non-conducting packings, fireproof material, cements, and cheaper glassware. L. J. S.

PUMPKIN, *Cucurbita Pepo* (Linn.). A plant growing in warm climates, yielding large fruits which are used as a vegetable and for stock feeding. Many varieties are known. Of the whole fruit, from 50 to 70 p.c. consists of rind and seeds, which are not edible. König gives as the average composition of the flesh—

Water	Protein	Fat	Sugar	Other N-free extract	Crude fibre	Ash
90·3	1·1	0·1	1·3	5·2	1·2	0·7

American analyses show a higher water content, 93 or 94 p.c.

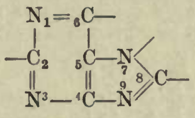
Pumpkin seeds contain from 25 to 35 p.c. of oil. Power and Salway (J. Amer. Chem. Soc. 1910, 32, 346) have examined the seeds with a view of discovering the constituent to which the action as a vermifuge, which the seeds possess, is due. They showed that no constituent of the seeds possessed any marked physiological activity and conclude that any medicinal value which they may have must be attributed to a mechanical effect. They found the seeds to consist of 20·8 p.c. of husks and 79.2 p.c. of kernels.

The entire seed yielded to light petroleum 34·3 p.c. of oil, which was optically inactive, had a sp.gr. of 0·9220 at 20°/20°, acid value 3·4, saponification value 189·4, iodine value 119·7. It consisted of the glycerides of linolic acid (45 p.c.), oleic acid (25 p.c.), and palmitic and stearic acids (30 p.c.), together with small quantities of a phytosterol $C_{27}H_{46}O$, m.p. 162°–163° and a similar substance, m.p. 140°.

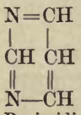
From the press cake, after removal of the oil, they obtained some soluble proteid material, sugar, traces of salicylic acid and of copper and about 0·06 p.c. of a resin, in which they found an acid, $C_{25}H_{51}O{\cdot}COOH$, m.p. 99°, soluble in hot alcohol and in ethyl acetate. It yielded an ethyl ester melting at 61°. Physiological tests with both the fatty oil and the resin, showed that neither possessed any value as a tænifuge. H. I.

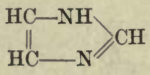
PURGATIN *v.* Synthetic drugs.

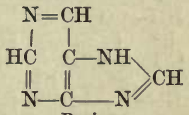
PURINES. The purines form a group of compounds, chiefly of animal or vegetable origin, containing the complex



which may be regarded as a combination of the two simpler ring compounds, the *pyrimidine* or *metadiazine* and the *iminazole* or *glyoxaline*

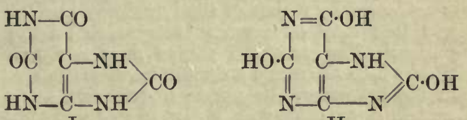

Pyrimidine.


Iminazole.


Purine.

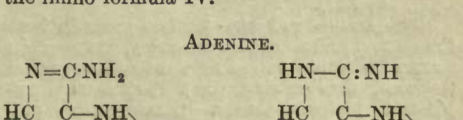
The name *purine* (from *purum* and *uricum*) was given by Fischer (Ber. 1898, 31, 2550) to the simplest member of the series, obtained from uric acid by a process of reduction. The naturally occurring purines contain hydroxyl or amino or methyl groups in place of the hydrogen atoms of the purine. For the hydroxyl substituted derivatives, the keto formula I. is more suitable than the tautomeric enolic formula II.

Uric Acid.

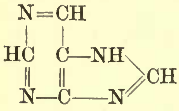

I. II.

whilst the amino formula III. is adopted for the amino substituted derivatives in preference to the imino formula IV.

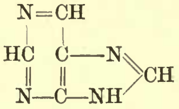
Adenine.


III. IV.

Purine itself is represented by the formula V. in preference to formula VI., and a similar convention is adopted in respect of its derivatives substituted in positions other than 7, 8, or 9.



V.

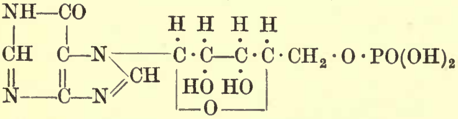


VI.

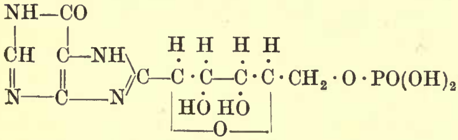
The source of the naturally occurring purines is the nucleoproteins of the cell nucleus. These are compounds of nucleic acids with different proteins, yielding, on partial hydrolysis, the protein and the nucleic acid. The nucleic acids are regarded as mono- or poly-nucleotides, *i.e.* compounds of phosphoric acid conjugated with a complex compound of a carbohydrate (hexose or pentose) and a base (purine or pyrimidine). The molecule of yeast nucleic acid

$$C_{38}H_{49}N_{15}P_4O_{29}$$

is composed of four such nucleotides (Levene and Jacobs, Ber. 1911, 44, 1027). The mononucleotide *inosic acid* $C_{10}H_{13}N_4PO_8$, is a compound of phosphoric acid, *d*-ribose and hypoxanthine, and can be represented by the formula



or



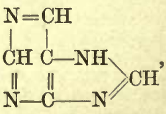
(Levene and Jacobs, *ibid.* 746).

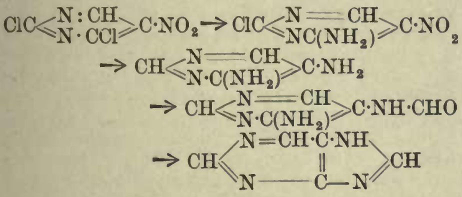
During metabolism the nucleoproteids undergo complete disruption, yielding the purine bases, guanine, adenine, xanthine and hypoxanthine; and the pyrimidine bases, thymine, cytosine and uracil. As a result of tissue metabolism, every normal adult excretes a certain characteristic amount (0·1 to 0·2 grms. daily) of purine substances which is independent of the diet, and this may be termed 'endogenous urinary purine.' On ordinary diet the amount is increased by a part of the 'nutrition purine' and this may be termed 'exogenous urinary purine.' The nutrition purine does not pass wholly into the urine, a certain fraction remains in the organism, the purine double ring being broken down; thus on a diet of calf's thymus that contains 0·4 p.c. of purine substances, the percentage of 'exogenous urinary purine' is 0·1 p.c. (Burian and Shur, Pflüger's Archiv. 1900, 80, 241).

The amino- and oxy- purines occur in both the animal and vegetable economy, but in plant tissues there are found also methyloxypurines (caffeine, theobromine, etc.). The methyloxypurines (heteroxanthine, paraxanthine) present in urine is part of the 'exogenous urinary purine' derived from a vegetable diet. Only a small proportion of the methyl purine present in the food is excreted unchanged, most of it undergoes demethylation by a process of oxidation and appears in the urine as a lower methylpurine.

Relation between the structure and the physical properties of the purines. The substitution of hydroxyl or the amino group for the hydrogen atoms of purine causes an increase in the melting-point and a diminution in the solubility of the compound: thus purine melts at 216°, 8-oxypurine at 317°, 6-aminopurine (adenine) at 360°. Purine is readily soluble, 6-oxypurine (hypoxanthine) dissolves in 69·5, 2:6-dioxypurine (xanthine) in 1400, 6:8-dioxypurine in 270, and trioxypurine (uric acid) in 1850 parts of boiling water; whilst 6-aminopurine (adenine) is very readily soluble in boiling water, 6-amino-2-oxypurine, 2-amino-6-oxypurine (guanine) and 2-amino-6:8-dioxypurine are very sparingly soluble, and 2:6-diamino-8-oxypurine is soluble in 350 parts of boiling water. The introduction of methyl groups causes a marked increase in the solubility and a lowering of the melting-point, thus whilst xanthine is soluble in 1400 parts of boiling water, and decomposes without melting, caffeine (1:3:7-trimethylxanthine) dissolves in 2 parts of boiling water, melts at 234°–235°, and sublimes with slight decomposition at 384°. The methyl substituted purines are also much more readily hydrolysed than those that are not so substituted, thus uric acid can be boiled with excess of normal alkali for a long time without undergoing much decomposition, but tetramethyluric acid is rapidly decomposed even in the cold, the mono-, di-, and tri-methyluric acids standing in intermediate position between the extremes. The position of the methyl groups in the compound also appears to affect the ease with which the decomposition occurs, the 1:3:9-trimethyluric acid, for example, is much more readily decomposed than the 1:7:9-derivative (Fischer, Ber. 1898, 31, 3266).

Physiological action of the purines. The action of caffeine and theobromine is twofold, in the first place they act on the central nervous system producing an increased sensibility to external stimulus, developing into tetanus as the dose is increased and culminating in paralysis when the dose is large. Secondly, they act on the muscles, facilitating the contraction of these at first, but producing muscular rigor when the dose is larger. Parallel with the action on the muscles is a diuretic action, the two increasing together. The nervous action depends on the presence of nitrogen in the molecule, for it is exhibited also by ammonia and its salts; the muscular action is characteristic of the purine ring. Purine itself exhibits both actions. Introduction of oxygen or alkyl groups affects the degree of the two actions both absolutely and relatively; no regularities could be observed in this respect, probably owing to the difference in solubility of the drugs. The introduction of alkyloxy groups produces a hypnotic or narcotic action which may almost mask the tetanus (Schmiedeberg, Ber. 1901, 34, 2550). For preparation of purine derivatives of therapeutic value, *cp.* Farbenfabriker vorm. Friedr. Bayer & Co. D. R. P. 209728.

Purine $C_5N_4H_4$, , was prepared by Fischer (Ber. 1897, 30, 2208, 2220; 1898, 31, 2550) from uric acid by the following series of reactions: potassium urate and phosphoryl chloride at 160°–170° yield 2:6-*dichloro*-8-*oxypurine*, which on further treatment with excess of the chloride at 150°–155°, is converted into 2:6:8-*trichloropurine*; when this is treated with hydriodic acid and phosphonium iodide at 0° it suffers partial reduction yielding 2:6-*di-iodopurine*, which is completely reduced to *purine* on boiling with zinc dust and water. The synthesis of purine has been effected by Isay (Ber. 1906, 39, 250) from nitrouracil, which is converted by phosphoryl chloride at 188° into 2:6-*dichloro-5-nitropyrimidine*; this yields 2-*chloro*-5-*nitro*-4-*aminopyrimidine* by the action of ammonia. On reduction with hydriodic acid and phosphonium iodide, 4:5-*diaminopyrimidine* is obtained. The 5-formyl derivative of this base loses water when heated above 198° yielding purine



Purine is a readily soluble crystalline compound, m.p. 216°–217° (corr.). It forms salts both with acids and bases; the *zinc* salt is very sparingly soluble; the *nitrate* $C_5N_4H_4{\cdot}HNO_3$ melts and decomposes at 205°; the yellow *picrate* $C_5N_4H_4{\cdot}C_6H_3N_3O_7$ melts at 208°. The base is very stable towards oxidising agents and in consequence does not give the murexide reaction. 2:6:8-*Trichloropurine* $C_5N_4HCl_3,5H_2O$ becomes anhydrous at 110°, melts with decomposition at 187°–189° (corr.), and dissolves in 70 parts of hot water. 2:6-*Diiodopurine* $C_5N_4H_2I_2$ melts at 224° with decomposition. 2:6-*Dichloro*-8-*oxypurine* $C_5N_4HCl_2O$ decomposes above 350° without melting, dissolves in 120 parts of boiling alcohol or 1000 parts of boiling water. It yields 8-*oxypurine* on reduction, m.p. 317° (corr.). 6-*Amino*-8-*oxy*-2-*chloropurine* is obtained by the action of ammonia on the dichloro compound; it carbonises above 360° without melting, and yields the base 6-*amino*-8-*oxypurine* on reduction; this is converted by nitrous acid into 6:8-*dioxypurine*, an isomeride of xanthine, m.p. above 400° with decomposition.

The following naturally occurring purines are described under their respective titles in other parts of this work:

Adenine, 6-*aminopurine*.
Guanine, 2-*amino*-6-*oxypurine*.
Hypoxanthine, 6-*oxypurine*.
Xanthine, 2:6-*dioxypurine*.
Heteroxanthine, 7-*methyl*-2:6-*dioxypurine*.
Paraxanthine, 1:7-*dimethyl*-2:6-*dioxypurine*.
Theophylline, 1:3-*dimethyl*-2:6-*dioxypurine*.
Theobromine, 3:7-*dimethyl*-2:6-*dioxypurine*.
Caffeine, 1:3:7-*trimethyl*-2:6-*dioxypurine*.
Uric acid, 2:6:8-*trioxypurine*.

M. A. W.

PURPLE, HESSIAN, *v.* AZO- COLOURING MATTERS.

PURPLE OCHRE (*Mars violet*) *v.* PIGMENTS.

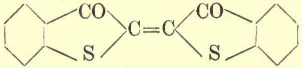
PURPLE OF CASSIUS *v.* GOLD PURPLE.

PURPLE OF MOLLUSCA *v.* PURPLE OF THE ANCIENTS; PUNICIN; INDIGO.

PURPLE OF THE ANCIENTS. The ancients derived their purple from certain molluscs or sea-snails, the *Purpura hæmastoma*, known to Pliny as *Buccinum*, and from the *Murex brandaris*, called by Pliny *Purpura*. At Athens and Pompeii, large quantities of the shells have been discovered lying in heaps close to ancient dyeworks. These molluscs are to be found throughout the whole of the Mediterranean, and, indeed, in the sea in numerous parts of the world varieties exist which may be employed for dyeing purposes. Two sorts of purple, known as Tyrian and Byzantium purple, were recognised by the ancients, the former possessing a redder tint than the latter.

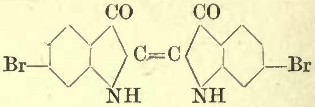
From the observations of Cole (Phil. Trans. 1685), Réaumur (Mem. de l'Acad. Royale des Sciences, 1711), and Bancroft (Philosophy of Permanent Colours, 1, 120, 1803), it appears that the colour-producing secretion, which resembles pus in appearance and consistence, is contained in a small whitish cyst or vein, placed transversely under, but in immediate contact with, the shell, and near the head of the animal. This pus-like matter, either diluted with water or undiluted, on being applied to bits of white linen or calico and exposed to sunlight rapidly changes its colour, passing from yellow, through light green, deep green, and 'watchet blue,' to purplish-red or crimson. To produce this change of colour the light of the sun is essential. It is effected more rapidly by the direct action of the sun's rays than by that of diffused light, but it does not take place in moonlight or in artificial light. If the linen or other fabric to which the secretion has been applied is kept in the dark, it remains unchanged, but when exposed to the sun it becomes purple, even after the lapse of years, though a little more slowly than at first. The metamorphosis which the change of colour indicates is not sensibly promoted by heat. It proceeds in a vacuum and in hydrogen or nitrogen gas as speedily as in air on exposure to light. The colour produced is remarkably stable, resisting the action of soap, alkalis, and most acids, being destroyed only by nitric acid and chlorine (*see* also Bizis, Journ. de Ch. Med. 1835, 10, 99, and A. and G. de Negri, Gazz. chim. ital. 1875, 437). Schunck (Chem. Soc. Trans. 1879, 35, 591), who examined the *Purpura capillus*, which he procured from the rocks at Hastings, finds that the colouring matter (punicin) is quite insoluble in water, alcohol, or ether, sparingly soluble in boiling benzene or boiling glacial acetic acid, and readily soluble in boiling aniline, giving a solution which is at first green, but as it approaches saturation becomes purplish-blue. At this point it shows a broad, well-defined absorption band, beginning near C and extending beyond D; but as the solution cools, depositing the substance contained in it, the colour changes to green, and the band becomes gradually narrower, until it occupies the space midway between C and D, and then disappears. The masses of colouring matter deposited from the solution in aniline are seen, under the microscope, to consist of star-shaped groups of irregular crystalline needles, which, when very thin, show by transmitted light a purple colour. Punicin is soluble in oil of vitriol, giving a dirty purple colour, and showing a broad ill-defined absorption-band between D and E, the green and blue of the spectrum being much darkened. On heating the solution slightly, or allowing it to stand for some time, the colour changes to a bright bluish-green and it now shows an absorption-band in the red. Punicin is also sparingly dissolved by a hot alkaline solution of stannous oxide, and the solution on exposure to air becomes covered with a blue pellicle. Punicin may be sublimed, giving crystals which show by reflected light a semi-metallic lustre, like that of sublimed indigo-blue (Schunck, *l.c.*). Witt (Technologie der Gespinnstfasern, 1888) expressed the opinion that the colouring matter yielded by these molluscs was an admixture of indigotin with a red colouring matter not so fast to light.

Friedländer (Annalen, 351, 390; Ber. 1906, 39, 1060) has examined the dye yielded by the *Murex brandaris* and *Murex trunculus* which he obtained from the zoological station at Trieste. Letellier (Compt. rend. 1891, 109, 82) had observed that, in addition to the colouring principle, organic sulphur compounds were also present in these glands, and it suggested itself, therefore, to Friedländer as possible that the 'purple of the ancients' might in reality consist of the thioindigotin



which he had lately discovered.

To isolate the colouring matter the glands of the molluscs were spread out as thinly as possible upon filter paper, which was then exposed to the sunlight for half an hour. The highly coloured product was now immersed in diluted hydrochloric acid (1 : 1), the mixture evaporated to dryness on the water-bath, the residue extracted with hot water, and washed with alcohol and ether. In this manner a product consisting only of cellulose and the pure colouring matter was obtained, and the latter could be readily removed by extraction with boiling anisole, from which it separates in the crystalline condition. Finally, it was recrystallised from nitrobenzene. It consists of dark violet crystals which possess a coppery lustre, dissolves in hot, high-boiling solvents with a blue-violet colour, yields a sublimate on heating, and in numerous respects resembles the colouring matter of the indigo group. Analysis indicated the absence of sulphur, although nitrogen was found to be present. The absorption spectrum is similar to that given by indigotin; but, on the other hand, it is distinguished from this latter colouring matter by its sparing solubility, and by giving with cold concentrated sulphuric acid a reddish-violet colouration. With fuming sulphuric acid it yields a soluble blue sulphonic acid, and when reduced in alkaline solution forms a pale yellow liquid, from which, when exposed to air, it separates as a reddish-violet precipitate. In a later paper by the same author (Ber. 1909, 42, 765) some slight modifications of the method for the isolation of the dye from the *Murex brandaris* are given, and it is shown that in this manner about 12,000 molluscs are required for the preparation of 1·4 grms. of the substance. This colouring matter contains bromine, and by a comparison with the synthetic dye there can be no doubt that it is in reality 6 : 6′-dibromoindigotin.

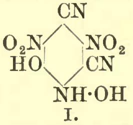


Further investigation has indicated that in addition to this dibromindigotin another dye of a bluer shade also containing bromine, but possessing a greater solubility in organic solvents, is produced from the *Murex brandaris.* It contains more carbon and less bromine than dibromindigotin, but its constitution is as yet undetermined (Friedländer, Chem. Zeit. 1911, 640).
A. G. P.

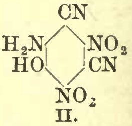
PURPURIC ACID *v.* MUREXIDE.

*iso***PURPURIC ACID.** When picric acid is added to a solution of potassium cyanide, the mixture becomes reddish-brown, and finally purple. Hlasiwetz (Annalen, 1859, 110, 289) first isolated the coloured compound and found it to be the potassium salt of an acid which he considered was isomeric with purpuric acid; he therefore gave it the name of iso*purpuric acid,* and prepared the ammonium, calcium, barium, lead, and silver salts by double decomposition (compare also Baeyer, J. 1858, 458). The potassium salt was formerly employed as a dye under the name *Grenat Brown.*

The *iso*purpurates are decomposed by the action of dilute nitric, sulphuric, or hydrochloric acid, but the free *iso*purpuric acid has been isolated from the ammonium salt by treating it with one equivalent of phosphoric acid at 0°; it is dark violet, and readily decomposed even by dissolving in water or in the ordinary organic solvents (Borsche and Böcker, Ber. 1904, 37, 4388). According to Borsche, the constitution of *iso*-purpuric acid is 2 : 4-dicyano-3 : 5-dinitro-6-hydroxy-β-phenylhydroxylamine I. (Ber. 1900, 33, 2719, 2995); but Nietzki and Petri (*ibid.* 1900, 33, 1788) regard it as an amino compound of the constitution 5-hydroxy-6-amino-2 : 4-dinitro*iso*phthalonitrile II.



I.



II.

The development of the characteristic colour of *iso*purpuric acid when picric acid is mixed with an alkali cyanide is commonly used as a test for cyanides. Reichard (Chem. Zeit. 1901, 25, 537) finds that 1 part of potassium cyanide in 2000 parts of water can be thus detected, although the development of the colour requires 24 hours; he also finds that the metallic cyanides, other than those of the alkalis, do not form purpurates with picric acid.

Test for cyanogenetic glucosides. Guignard (Compt. rend. 1906, 142, 545) has used the reaction as a delicate test for the presence of prussic acid among the products of hydrolysis of substances containing cyanogenetic glucosides. Using test-papers prepared from sodium picrate, exposed to the action of the gaseous products of hydrolysis of the material under investigation, the presence of 0·00005 grm. of prussic acid can be detected after 12 hours', and 0·00002 grm. after 24 hours' exposure.

*meta***Purpuric acid.** Potassium cyanide forms purple compounds when added to a nitrophenol containing at least two nitro groups in the molecule, which must be in the *meta* position to one another, and at least one of them *ortho* to the hydroxyl group. The compound formed by the interaction of potassium cyanide and 2 : 4-dinitrophenol is the salt of *metapurpuric acid*, and is the *potassium salt of* 4-*nitro*-2-*hydroxylamino*-3-*cyanophenol*, it forms dark red needles, fairly readily soluble in water or acetic acid, sparingly so in acetone or alcohol, melts and decomposes above 250°, and yields barium, strontium, copper, and silver salts by double decomposition. It is oxidised by the action of dilute nitric acid or potassium hypobromite yielding 2 : 6-dinitro-3-hydroxybenzonitrile. *meta*Purpuric acid can be prepared from the ammonium salt by treating it with one equivalent of phosphoric acid in aqueous solution at 0° ; it is a dark red powder, decomposes at 92°, yielding nitric oxide (Pfaundler and Oppenheim, Zeitsch. Chem. 1865, 470; Sommaruga, Annalen, 1871, 157, 335; Borsche, Ber. 1900, 33, 2718, 2723; Borsche and Böcker, *ibid.* 1903, 36, 4357; 1904, 37, 1843, 4388; Borsche and Gahrtz, *ibid.* 1905, 38, 3538; 1906, 39, 3359; Borsche and Heyde, *ibid.* 1905, 38, 3938).

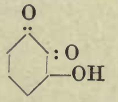
PURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

PURPUROGALLIN $C_{12}H_8O_5$. By treating pyrogallol in acid solution with silver nitrate or potassium permanganate, A. Girard (Ber. 1869, 2, 562) obtained a red substance $C_{20}H_{16}O_9$, which he named purpurogallin. A. Wichelhaus (Ber. 1872, 5, 848), by oxidising pyrogallol with quinone, obtained the same substance (pyrogallol quinone), and gave it the formula $C_{18}H_{14}O_9$ and the constitution $(OH)C_6H_3[O{\cdot}O{\cdot}C_6H_3(OH)_2]_2$. Struve (Annalen, 1872, 163, 102) made the interesting discovery that purpurogallin is formed by allowing a mixture of pyrogallol and gum arabic solutions to stand in contact with air for some hours. On repeating these experiments, Clermont and Chautard (J. 1882, 682) succeeded in obtaining a yield of 67 p.c. of purpurogallin by the gum arabic method. These authors also employed platinum black as oxidising agent, and observed the production of carbon dioxide during the formation of purpurogallin; they describe a tetra-acetyl derivative $C_{20}H_{12}O_9(C_2H_3O)_4$, m.p. 186°, sodium and barium salts $C_{20}H_{12}Na_4O_9$, $C_{20}H_{12}Ba_2O_9$, and a tetrabromo compound $C_{20}H_{12}Br_4O_9$, m.p. 202°–204°. Heated with sulphuric acid, purpurogallin gave the compound $C_{20}H_{12}O_{10}$, and by means of hydriodic acid a mixture of hydrocarbons $(C_{10}H_{14})_n$ was formed. S. Hooker (Ber. 1887, 20, 3259) employed potassium ferricyanide as the oxidising agent, the yield being 13 to 14 p.c., and also prepared purpurogallin by the action of potassium nitrite on a solution of gallic acid in the cold. Nietzki and Steinmann (*ibid.* 1887, 20, 1277) obtained the best yields of purpurogallin by treating a well-cooled aqueous solution of pyrogallol acidified with acetic acid, with sodium nitrite, and were indebted for this method to a private communication from Nölting. As by distillation with zinc dust purpurogallin was found to yield naphthalene, it seemed evident that such a nucleus pre-exists in this compound, and it was considered likely that during the oxidation of the pyrogallol some of the benzene nuclei are split up, and that condensation of the product ensues to form this naphthalene ring. Acetyl purpurogallin was again examined, and the formula $C_{20}H_{16}O_9$ considered as probably representing the colouring matter itself.

Perkin and Steven (Chem. Soc. Trans. 1903, 83, 192) obtained from pyrogallol by means of potassium ferricyanide (Hooker, *l.c.*) only 14 p.c. of purpurogallin, whereas the nitrous acid method (Nietzki and Steinmann) gave from 20 to 32·5 p.c. In the latter case, 20 grms. of pyrogallol dissolved in 300 c.c. of water were treated with 8 c.c. of glacial acetic acid, the solution cooled by addition of ice, and slowly treated with 8 grms. of sodium nitrite shaking well after each addition. The precipitate of purpurogallin was removed after an hour, and the filtrate allowed to stand overnight, as frequently a further quantity of the colouring matter then separated.

A. G. Perkin and F. M. Perkin (Chem. Soc. Trans. 1904, 85, 243) obtained purpurogallin by the electrolytic oxidation of pyrogallol in the presence of a 15 p.c. solution of sodium sulphate, employing a rotating anode. Satisfactory results were also obtained when, instead of rotating the anode, a rapid stream of air was blown through the mixture, the yield thus averaging from 36·4 to 37 p.c.

When pyrogallol in alcoholic solution is treated with acetic acid and *iso*amyl nitrite, it gives a compound $C_6H_4O_3$ or $C_{12}H_8O_6$, colourless prismatic needles, m.p. 206°–208° in minute amount, the acetyl derivative of which melts at 283°–285° (P. and S. Chem. Soc. Trans. 1906, 89, 802). As on reduction with zinc dust and acetic acid pyrogallol is regenerated, it is possible that this substance is hydroxy-*o*-benzoquinone



Digested with boiling water, purpurogallin, a soluble compound $C_{12}H_{10}O_7$(?), m.p. 242°–243°, and a brown resin are produced. and this result renders it not improbable that the compound $C_6H_4O_3$ represents an intermediate stage in the formation of purpurogallin from pyrogallol by the ordinary methods. Wichelhaus (*l.c.*), indeed, predicted that the first product of the oxidation of pyrogallol by his methods is a hydroxy-quinone.

Ruzicka (Monatsh. 1910, 31, 799), who experimented with the gum arabic method of Clermont and Chautard (*l.c.*), could obtain only a 24 p.c. yield of purpurogallin in this manner.

Perkin and Steven, as the result of cryoscopic determinations, consider that the molecular weight of purpurogallin is best expressed by the formula $C_{11}H_8O_5$, and show that the acetyl and bromine derivatives described by Clermont and Chautard should be respectively represented as $C_{11}H_4O_5(C_2H_3O)_4$ and $C_{11}H_6Br_2O_5$.

When purpurogallin is methylated by means of methyl iodide *purpurogallin trimethyl ether* $C_{11}H_5O_2(OCH_3)_3$, orange-yellow needles, m.p. 174°–177°, which yields the acetyl derivative $C_{11}H_4O_2(OCH_3)_3C_2H_3O$ colourless needles, m.p. 140°–143°, is produced. A considerably better yield can be obtained by the employment of methyl sulphate (Perkin, Chem. Soc. Trans. 1912, 101, 803), whereas, according to Ruzicka (*l.c.*), diazomethane quantitatively converts purpurogallin into the trimethyl compound. Digested with alcoholic potash at 170°, purpurogallin trimethyl ether gives a small quantity of an acid $C_{13}H_{12}O_5$ (P. and S.) $C_{11}H_6O_3(OCH_3)_2$ (R.), m.p. 197°–199° (Chem. Soc. Proc. 1905, 21, 211), which is in reality *purpurogallone dimethyl ether.* Strongly heated, it yields a sublimate which is an anhydride, m.p. 164°–166°, and the same compound is formed with boiling acetic anhydride.

By the action of methyl sulphate and alkali on the trimethyl compound *purpurogallin-tetramethyl ether* $C_{11}H_4O(OCH_3)_4$, prisms, m.p. 93°–95° (P.), 91°–92° (R.) is produced, and from this, by means of alcoholic potash at 170°, a small amount of an acid can be obtained.

When purpurogallin is digested with 50 p.c. aqueous potassium hydroxide at about 170°, iso*purpurogallone* $C_{22}H_{16}O_{10}$, yellow prismatic needles (m.p. above 300°), and *purpurogallone* $C_{11}H_8O_5$, m.p. 262°–264°, are obtained. Distilled with zinc dust the latter compound gives naphthalene, and when digested with hydriodic acid (sp.gr. 1·7) among other substances *β-naphthol* and 2 : 3-*dihydroxynaphthalene* are produced (Chem. Soc. Trans. 1912, 101, 803). Sulphuric acid converts *iso*purpurogallone into *anhydro*-iso-*purpurogallone* $C_{22}H_{10}O_8$, yellow prisms (m.p. above 310°), and with acetic anhydride *acetyl-anhydro* - iso*purpurogallone* $C_{22}H_8O_8(C_2H_3O)_4$ colourless needles, m.p. 280°–282°, is produced. iso*Purpurogallone tetramethyl ether*, colourless needles, m.p. 211°–213°, can be prepared by means of methylsulphate. Whereas purpurogallone is a trihydroxynaphthalene carboxylic acid, *iso*purpurogallone is the corresponding dinaphthyl compound (*loc. cit.* 1912).

Purpurogallin carboxylic acid $C_{11}H_7O_5\cdot COOH$, orange-red needles (m.p. above 330°), is obtained in small quantity by oxidising gallic acid in aqueous solution with potassium ferricyanide in the presence of potassium or sodium acetate. Much larger amounts are, however, produced by the electrolytic oxidation of gallic acid (A. G. and F. M. Perkin, Chem. Soc. Trans. 1908, 98, 1186) employing sodium sulphate (yield 34 p.c.) or sodium acetate (yield 30–40 p.c.) as electrolytes. *Sodium purpurogallin carboxylate*

$$C_{12}H_7O_7Na,4H_2O$$

orange-brown leaflets; *potassium purpurogallin carboxylate* $C_{12}H_7O_7K,3H_2O$, orange-red prismatic needles; and *barium purpurogallin carboxylate* $(C_{12}H_7O_7)_2Ba$ needles; *methylpurpurogallin carboxylate tetramethyl ether*

$$C_{11}H_3O(OMe)_4CO_2Me$$

colourless needles, m.p. 120°–121°; and *purpurogallin carboxylic acid tetramethylether*

$$C_{11}H_3O(OMe)_4COOH$$

needles, m.p. 182°–183°, have been prepared.

Boiling aqueous potassium hydroxide (50 p.c.) converts purpurogallin carboxylic acid into *purpurogallone carboxylic acid* $C_{12}H_8O_7,2H_2O$ yellow needles (m.p. above 300°), which gives *acetyl-anhydro-purpurogallone carboxylic acid*

$$C_{12}H_4O_6(C_2H_3O)_2$$

colourless needles, m.p. 236°–238°; *methyl-purpurogallone carboxylate tetramethyl ether* $C_{11}H_3O(OMe)_4CO_2Me$, colourless prisms, m.p. 110°–111°; and *purpurogallone carboxylic acid tetramethyl ether* $C_{11}H_3O(OMe)_4COOH$, needles, m.p. 166°–167°.

Purpurogallin and purpurogallin carboxylic acid are powerful dyestuffs, whereas the purpurogallones and purpurogallone carboxylic acid possess a similar property, although in a less marked degree. On mordanted wool the following shades are produced :—

	Chromium	*Aluminium*	*Tin*	*Iron*
Purpurogallin . .	Reddish chocolate brown	Brownish red	Brick red	Deep black
Purpurogallin carboxylic acid . .	Reddish brown	Reddish puce	Brick red	Brownish black
Purpurogallones . Purpurogallone carboxylic acid . .	Chocolate brown	Pale chocolate brown	Pale yellow	Chocolate brown

The fact that purpurogallin on distillation with zinc dust gives naphthalene suggests that this colouring matter is a *β*-naphthoquinone derivative, in which, owing to the ready oxidisability of its alkaline solution, a pyrogallol nucleus is present. On the other hand, its exact structure has not yet been determined. A. G. P.

PURPUROXANTHIN 1 : 3 - *Dioxyanthraquinone v.* ALIZARIN AND ALLIED COLOURING MATTERS.

PURREE, PIURI, or **PIOURY,** *v.* INDIAN YELLOW.

PUTREFACTION *v.* FERMENTATION.

PUTTY POWDER. *Stannic oxide.* Common qualities of putty powder are produced by skimming the surface of boiling tin, the scum so obtained being then freed from foreign matter and well washed and ground. The better kinds are obtained by treating tin with nitric acid, thus forming stannic oxide. It is used in enamelling to give an opaque white colour : it is also employed for polishing. (*V.* TIN SALTS AND OXIDES.)

PUZZUOLANA *v.* CEMENTS.

PYKNOMETER *v.* SPECIFIC GRAVITY.

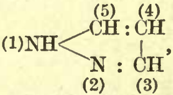
PYRAMIDON *v.* SYNTHETIC DRUGS.

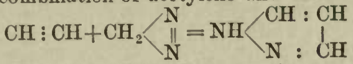
PYRANTHRENE *v.* INDANTHRENE.

PYRANTIN. Trade name for *p*-ethoxyphenyl-succinimide $[CH_2\cdot CO]_2N\cdot C_6H_4\cdot OC_2H_5$, prepared by fusing the hydrochloride of *p*-aminophenetole or phenacetin with succinic acid. Forms colourless prismatic needles, m.p. 155°. Used as a febrifuge (Piutti, J. Pharm. Chim. 16, 298). *V.* SYNTHETIC DRUGS.

PYRARGYRITE, or dark-red silver-ore (Ger. *Dunkles Rothgiltigerz ;* Span. *Rosicler obscuro*). Silver sulphantimonite, Ag_3SbS_3, crystallised in the rhombohedral system. Well-formed crystals are not uncommon ; these are black with a metallic-adamantine lustre, but thin splinters are translucent and dark red. The purplish-red streak serves to distinguish pyrargyrite from the closely allied mineral proustite (*q.v.*). Hardness, 2½, sp.gr. 5·85. It occurs in metalliferous veins, and is occasionally found in sufficient amount to be of importance as an ore of silver (Ag 59·9 p.c.) ; *e.g.* formerly at Andreasberg in the Harz mountains ; at Guanajuato in Mexico ; and at Colquechaca in Bolivia. L. J. S.

PYRAZINE *v.* AZINES.

PYRAZOLE $C_3H_4N_2$ has the structural formula , the orientation of radicles within the ring being designated by the numbers as shown. It is isomeric with glyoxaline or iminazole, and is sometimes termed α-pyrazole to distinguish it from its isomerides, which are known as β-pyrazoles. Pyrazole has been prepared by a variety of methods: thus by the direct combination of acetylene and diazomethane



$$CH\vdots CH+CH_2\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. = NH\left\langle\begin{matrix}CH : CH\\ |\\ N : CH\end{matrix}\right.$$

(Pechmann, Ber. 1898, 31, 2950); by the condensation of epichlorhydrin with hydrazine hydrate in presence of zinc chloride (Balbiano, *ibid.* 1890, 23, 1105); by the oxidation of a chloroform solution of pyrazoline with bromine (Curtius and Wirsing, J. pr. Chem. 1894, [ii.] 50, 544); but it is, perhaps, most conveniently prepared by heating pyrazole di- or tri-carboxylic acid or its ester to 230°–240°. The latter is itself readily obtained from ethyl diazoacetate by heating it with dimethyl acrylic ester for two hours on a water-bath. The purified 3 : 4 : 5-pyrazoline tricarboxylic ester so obtained is then heated with 1 molecule bromine in chloroform solution when it is converted into ethyl 3 : 4 : 5-pyrazole tricarboxylate, m.p. 71° (anhydrous, 91°). On saponification the free acid is formed and decomposes at 233° (Buchner and Heide, Ber. 1901, 34, 347).

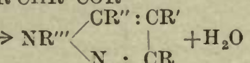
Pyrazole crystallises in long needles, m.p. 70°, b.p. 187°, and is readily soluble in water. It is more stable and basic in character than pyrrole, and it has the general properties of an aromatic substance (Knorr, *ibid.* 1895, 28, 715). It also resembles pyridine in its double salts with a number of metallic chlorides and sulphates, and in the properties of its alkyl derivatives. It forms salts with the halogen, sulphuric, and picric acids (Buchner and Fritsch, Annalen, 1893, 273, 257; Mandalà, Gazz. chim. ital. 1910, 40, i. 117). When reduced it forms pyrazoline.

Treated with fuming sulphuric acid it yields a *sulphonate* (Eppler, Zeitsch. Krist. 1898, 29, 233). *Halogen* (Knorr, *l.c.*; Ber. 1904, 37, 350; Buchner and Fritsch, *l.c.*; Mazzara and Borgo, Atti. R. Accad. Lincei, 1906, [v.] 15, i. 704), *nitro* (Hell and Torrey, Amer. Chem. J. 1899, 22, 105; Buchner, Annalen, 1893, 273, 217; Knorr, *ibid.* 1894, 279, 278), *amino* (Knorr, Ber. 1895, 28, 715), and *nitro halogen* (Black and Hill, Amer. Chem. J. 1905, 33, 292) derivatives have been obtained.

Pyrazole forms a large number of alkyl derivatives, the following being some of the general methods for their synthesis :—

(1) β-Diketones or β-ketonealdehydes of the general formula $R{\cdot}CO{\cdot}CHR'{\cdot}COR''$ (R, R′, R′ are positive or negative radicles or hydrogen) react with hydrazine or its primary aromatic derivatives, yielding hydrazones which readily undergo further condensation forming pyrazole derivatives, thus :—

$$NHR'''{\cdot}NH_2+COR{\cdot}CHR'{\cdot}COR'' =H_2O+NHR'''{\cdot}N : CR{\cdot}CHR'{\cdot}COR''.$$



$$NHR'''{\cdot}N : CR{\cdot}CHR'{\cdot}COR'' \rightarrow NR'''\left\langle\begin{matrix}CR'' : CR'\\ |\\ N : CR\end{matrix}\right. +H_2O$$

This is the best and most general method (Knorr, Annalen, 1887, 238, 137; *see* also D. R. P. 33536; Knorr and Blanks, Ber. 1885, 18, 311, 2256; Claisen and Roosen, *ibid.* 1891, 24, 1888).

(2) Hydrazine also reacts with ketones of the formula $R{\cdot}C\vdots CO{\cdot}R'$, and with aldehydes and ketones of formula $R{\cdot}CO{\cdot}CR' : CHR''$, to form pyrazoles and pyrazolines (Moureu and Brachin, Compt. rend. 1903, 136, 1262).

Pyrazoles containing an alkyl group attached to nitrogen are obtained by treating silver pyrazole with alkyl iodide or by distilling an alkyl iodide of the pyrazole (Knorr, Ber. 1895, 28, 716).

(3) Pyrazolecarboxylic esters may be formed by the action of diazoacetic ester on acetylenedicarboxylic ester (Buchner, Annalen, 1893, 273, 214).

(4) According to Stoermer, pyrazoles may be obtained almost in theoretical yield by the reduction of the pyrazolones with phosphorus tribromide (Ber. 1907, 40, 484; Annalen, 1907, 352, 322).

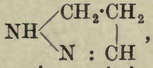
(5) Lactones of the pyrazole series may be prepared by condensing pyrazolones with alkyl acetoacetates (Wolff and Schreiner, Ber. 1908, 41, 550; Bulow and Schaub, *ibid.* 1945).

(6) Pyrazole derivatives may be synthesised by condensing the phenylhydrazone of benzaldehyde or its derivatives with ethyl acetoacetate in presence of zinc chloride (Minunni, Atti. R. Accad. Lincei, 1905, [v.] 14, ii. 414; *ibid.* 1906, [v.] 15, i. 19, 136).

(7) Pyrazole compounds containing acid groups attached to nitrogen can be obtained by condensing the sodium derivatives of 5-chloro-3-methyl- and 5-chloro-3-phenylpyrazoles with halogenated fatty esters (Michaelis and Schmidt, Ber. 1910, 43, 2116).

Intensely fluorescent pyrazole derivatives have been prepared by heating 4-hydrazino-1-hydroxyanthraquinone hydrochloride with aniline and aniline hydrochloride, and also by heating dihydrazinoanthraquinone or 1 : 5-disulphohydrazinoanthraquinone with hydrochloric acid (D. R. P. 171293).

The diazopyrazoles readily couple with phenols forming azo dyestuffs. When the pyrazoles obtained from phenylhydrazines are reduced with sodium and alcohol they form pyrazolines



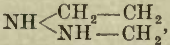
$$NH\left\langle\begin{matrix}CH_2{\cdot}CH_2\\ |\\ N : CH\end{matrix}\right.$$

, which on oxidation with chromic or nitric acid, or with ferric chloride in acid solution form red or blue colouring matters (Knorr, Ber. 1893, 26, 100).

The alkyl derivatives of pyrazole are too numerous to be described in detail.

Literature.—Buchner and others, Ber. 1902, 35, 31, 34, 37; Eng. Pat. 22064, 1904; J. Soc. Chem. Ind. 1905, 43; Michaelis and Behn, Ber. 1900, 33, 2595; Michaelis and Hepner, *ibid.* 1903, 36, 3271; Sachs and Alsleben, *ibid.* 1907, 40, 664; Wislicenus and Breit, Annalen, 1907, 356, 32; Michaelis and Klopstock, *ibid.* 354, 102; Auwers, *ibid.* 1911, 378, 210; Michaelis, *ibid.* 293; Michaelis and Lochwitz, Ber. 1910, 43, 2106; Bülow, *ibid.* 1911, 44, 601; Bauer and Dieterle, *ibid.* 2697; Mohr, J. pr. Chem. 1909, [ii.] 79, 1; amongst others.

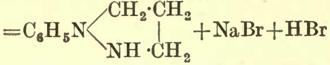
PYRAZOLIDINES



$$NH\left\langle\begin{matrix}CH_2-CH_2\\ NH-CH_2\end{matrix}\right.,$$

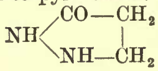
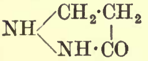
the parent substance is not known, and the derivatives, too, although numerous, have been little investigated owing to their instability. They may be obtained by the action of sodium phenylhydrazine or its derivatives on trimethylene bromide

$C_6H_5NH{\cdot}NHNa+CH_2Br{\cdot}CH_2{\cdot}CH_2Br$

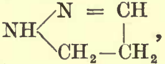


$$=C_6H_5N<\begin{array}{l}CH_2{\cdot}CH_2\\ \quad\ |\\ NH{\cdot}CH_2\end{array}+NaBr+HBr$$

(Michaelis and Lampe, Annalen, 1893, 274, 317; *see* also Tafel and Pfeffermann, Ber. 1903, 36, 221; Buchner and Perkel, *ibid.* 3774; Prager, *ibid.* 1452; Japp and Michie, Chem. Soc. Trans. 1903, 307). They are energetic reducing agents, and are readily oxidised to pyrazolines.

PYRAZOLIDONE  $NH<\begin{array}{l}CO-CH_2\\ \qquad|\\ NH-CH_2\end{array}$ or  $NH<\begin{array}{l}CH_2{\cdot}CH_2\\ \quad\ |\\ NH{\cdot}CO\end{array}$ is obtained by agitating hydrazine hydrate with acrylic acid in the cold. It has b.p. 134°, is insoluble in soda and is readily transformed into pyrazolone by oxidation (Rothenburg, J. pr. Chem. 1887, [ii.] 51, 72).

The 3- and the 5- derivatives may be obtained by condensing phenyl or other derivative of hydrazine with acrylic, crotonic, propionic, butyric, or other acids and their derivatives (Rothenburg, Ber. 1893, 26, 2994; Knorr and Duden, *ibid.* 108; Stolz, *ibid.* 1895, 28, 630; Kopisch, *ibid.* 1894, 27, 3111; Harries and Loth, *ibid.* 1896, 29, 517; Prentice, Chem. Soc. Trans. 1904, 1667; Japp and Mayland, *ibid.* 1490; *see* also Michaelis and Schenk, Ber. 1907, 40, 3568; Bulow and Weedlich, *ibid.* 4326; Muckermann, *ibid.* 1909, 42, 3449).

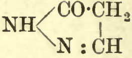
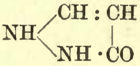
PYRAZOLINE  $NH<\begin{array}{l}N\ =\ CH\\ \qquad|\\ CH_2-CH_2\end{array}$, may be obtained by dropping an ethereal solution of acrolein (1 mol.) into an ethereal solution of hydrazine (a little over 1 mol.). The ether is then evaporated, the residue saturated with concentrated hydrochloric acid at 70°, filtered, and evaporated. The salt is dissolved in absolute alcohol, reprecipitated with ether and decomposed with potash (Curtius and Wirsing, J. pr. Chem. 1894, [ii.] 50, 538). Pyrazoline is a liquid, b.p. 144°, evolves ammonia when boiled with potash, and is oxidised to pyrazole when treated with bromine. It forms a *hydrochloride*, m.p. 130°, a *platinichloride*, and a *picrate*, m.p. 130°.

Its derivatives may be obtained as above (Fischer and Knoevenagel, Annalen, 1887, 239, 197); also by the reduction of the corresponding pyrazole, pyrazolidone, or pyrazolidine; by treating the hydrazones of unsaturated aldehydes and ketones containing a double linking in the α- position, with hot glacial acetic acid (Auwers and Müller, Ber. 1908, 41, 4230; Auwers and Voss, *ibid.* 1909, 42, 4411), and by the action of unsaturated ketones on diazomethane (Azzarello, Atti. R. Accad. Lincei. 1905, [v.] 14, ii. 229).

For the various derivatives, *see* Klages, J. pr. Chem. 1902, [ii.] 65, 387; Balbiano, Gazz. chim. ital. 1888, 81, 371; Knorr, Ber. 1893, 26, 102, 108; *ibid.* 1895, 28, 712; Harries, Annalen, 1901, 319, 233; Buchner and Schröder, Ber. 1902, 35, 789; Moureu and Lazennec, Compt. rend. 1906, 143, 1239; Maire, Bull. Soc. chim. 1908, iv. 3, 272, amongst others.

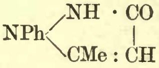
The pyrazolines are much more unstable than the pyrazoles, the parent substance pyrazoline being the most stable. They behave as weak bases and have many of the properties of unsaturated aliphatic compounds, of hydrazones and of aldazines.

With oxidising agents many of them yield characteristic red or blue dyestuffs.

PYRAZOLONE $C_3H_4N_2O$ can exist in the two modifications  $NH<\begin{array}{l}CO{\cdot}CH_2\\ \quad\ |\\ N:CH\end{array}$ (5-pyrazolones) and  $NH<\begin{array}{l}CH:CH\\ \quad\ |\\ NH{\cdot}CO\end{array}$ (3-pyrazolones) and many derivatives of each of these have been obtained.

3-Pyrazolone is only known in the form of its derivatives which may be readily obtained by the condensation of acetoacetic ester and acetyl- or benzoyl-phenyl hydrazine in the presence of phosphorus trichloride (Mayer, Ber. 1903, 36, 717).

1-Phenyl-5-methyl-3-pyrazolone

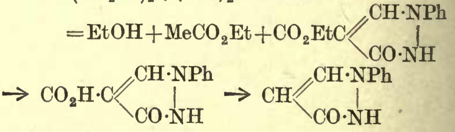


$$NPh<\begin{array}{l}NH\ \cdot CO\\ \qquad\ |\\ CMe:CH\end{array}$$

m.p. 166°, b.p. 344°–345°, is best obtained by the action of phosphorus pentachloride on a mixture of acyl phenyl hydrazine and ethyl acetoacetate (Michaelis, Annalen, 1905, 338, 267). It has both acid and basic properties, and with phosphorus oxychloride, yields 3-chloro-1-phenyl-5-methyl pyrazole, m.p. 295°. It also exists in a labile form, m.p. 157°, and gives a number of acyl and other derivatives.

By condensing ethyl ethoxymethylenemalonate with acetyl phenylhydrazine in the presence of phosphorus tri- or oxy-chloride, a product is produced which, when saponified, yields 1-*phenyl*-3-*pyrazolone carboxylic acid*, m.p. 216°. This on distillation loses carbon dioxide, forming 1-*phenyl*-3-*pyrazolone*, glistening leaflets, m.p. 155°–156° (Michaelis and Remy, Ber. 1907, 40, 1020).

$OEtCH(CO_2Et)_2+(NH)_2PhCOMe$



$$=EtOH+MeCO_2Et+CO_2EtC<\begin{array}{l}CH{\cdot}NPh\\ \qquad|\\ CO{\cdot}NH\end{array}$$

$$\rightarrow CO_2H{\cdot}C<\begin{array}{l}CH{\cdot}NPh\\ \qquad|\\ CO{\cdot}NH\end{array}\rightarrow CH<\begin{array}{l}CH{\cdot}NPh\\ \qquad|\\ CO{\cdot}NH\end{array}$$

1-Aryl-3- or 5-halogen methyl-2 : 4-dialkyl-3-pyrazolones have been obtained by the action of a halogen on the corresponding 5-pyrazolone when a dihalide is formed, from which on elimination of halogen hydride, the 3-pyrazolone is produced (D. R. P. 208593).

The 3-pyrazolones differ from the 5-isomerides in yielding with sodium nitrite green nitroso derivatives, which, on reduction, yield stable amino derivatives, whereas the 5-pyrazolones yield red-yellow *iso*nitroso derivatives, which on reduction yield unstable amino-pyrazolones. The 3-pyrazolones only react in the hydroxylic form, but the 5-pyrazolones sometimes behave as carbonyl compounds. For many 3-pyrazolone derivatives, *see* Michaelis, Annalen, 1906, 350, 288; *ibid.* 1907, 358, 127; *ibid.* 1910, 373, 129; Kümmel and Remy, Zeitsch. Elektrochem. 1909, 15, 254; Mauthner, Ber. 1908, 41, 2532).

5-Pyrazolone is prepared by heating together hydrazine sulphate (13 parts), sodium formylacetate (20 parts), and caustic soda (200 parts) to 100°. The mixture is acidified with sulphuric acid, rapidly evaporated and extracted with boiling alcohol. The extract is evaporated, redissolved in absolute alcohol and precipitated with ether (Knorr, Ber. 1896, 29, 253). It may also be prepared by the distillation of pyrazolone carboxylic acid (Ruhemann and Morrell, *ibid.* 1895, 28, 988). 5-Pyrazolone forms needle-shaped crystals, m.p. 165°. It sublimes with decomposition, is soluble in water and in alcohol, reduces ammoniacal silver solution, and gives a brown-red colour with ferric chloride.

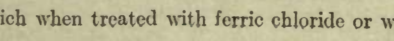
Pyrazolones may be synthesised by the interaction of hydrazine with acetylenic amides, ammonia being eliminated, thus from phenylpropiolamide $C_6H_5\,C{\vdots}C{\cdot}CONH_2$ a *phenyl pyrazolone*, m.p. 237°, is obtained; the same product is obtained from the esters of phenylpropiolic or benzoylacetic acids. An *amylphenyl pyrazolone*, m.p. 96°, is obtained by condensing phenyl hydrazine with either ethyl amyl propiolate or caproylacetate. Similarly ethylhexylpropiolate and heptylacetate give an identical *hexylphenylpyrazolone*, m.p. 84°–85°. Pyrazolones are also formed by the interaction of hydrazine or phenyl hydrazine with alkylated β-hydroxyacrylic esters (Moureu and Lazennec, Compt. rend. 1906, 142, 1534).

Pyrazolone derivatives are also formed by the interaction of β-halogen substituted fatty acids or their esters with phenyl hydrazine (Eng. Pat. 9923, 1891; J. Soc. Chem. Ind. 1891, 793; *ibid.* 1893, 463), or by the action of acetyl phenyl hydrazine on malonic acid and its alkyl derivatives in presence of phosphorus trichloride (Michaelis and Schenk, Ber. 1907, 40, 3568; Conrad and Zart, *ibid.* 1906, 39, 2282).

Compounds belonging to the pyrazolone group have been obtained by the action of hydrazine hydrate on dimethylpyrone dicarboxylate (Palazzo and Liverani, Atti. R. Accad. Lincei, 1911, [v.] 20, ii. 55).

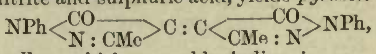
Of the large number of 5-pyrazolones known, the following may be mentioned:—

1-Phenyl-3-methyl-5-pyrazolone is obtained by the action of phenylhydrazine or its hydrochloride on ethyl acetoacetate (Knorr, Ber. 1883, 16, 2597), and by various other methods (*ibid.* 1894, 27, 1175; D. R. PP. 32277; 77174; Frdl. 1877–87, i. 213; *ibid.* 1894–97, iv. 1198; Bougert, Compt. rend. 1901, 132, 974). It forms prismatic crystals, m.p. 127°, b.p. 287°/205 mm., and unites with both acids and bases. It condenses with ketones, with hydroxy aldehydes (Tambor, Ber. 1900, 33, 864), with diazotised primuline to form azo colouring matters (D. R. P. 117575; *see* also D. R. P. 134162), and is also employed in the manufacture of antipyrine. It forms a large number of derivatives, but unlike antipyrine, it does not combine with phenols or hydroxy acids (Patein, Compt. rend. 1897, 124, 234). When boiled with excess of phenyl hydrazine or when the silver salt is treated with iodine, it is converted into bis-phenylmethylpyrazolone



$$\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{CO}\text{———}\\ \mathrm{N:CMe}\end{array}\Big\rangle\mathrm{CH:CH}\Big\langle\begin{array}{r}\text{———}\mathrm{CO}\\ \mathrm{CMe:N}\end{array}\Big\rangle\mathrm{NPh}$$

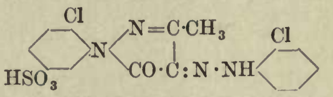
which when treated with ferric chloride or with sodium nitrite and sulphuric acid, yields *pyrazole blue*



$$\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{CO}\text{———}\\ \mathrm{N:CMe}\end{array}\Big\rangle\mathrm{C:C}\Big\langle\begin{array}{r}\text{———}\mathrm{CO}\\ \mathrm{CMe:N}\end{array}\Big\rangle\mathrm{NPh},$$

violet needles, which resemble indigo in constitution and many properties, but is not so stable, and is of no tinctorial value (Knorr, Annalen, 1887, 238, 171; Knorr and Duden, Ber. 1892, 25, 765). Pyrazole blue is also formed by the direct oxidation of the pyrazolone with ferric chloride (Feist, Annalen, 1906, 345, 100).

1-*o*-Chlorophenyl-3-methyl-5-pyrazolone-*m*-sulphonic acid combines with diazo-*o*-chloroaniline, forming the dyestuff



The latter may also be produced by other methods and dyes unmordanted wool fast clear yellow shades (U.S. Pat. 982050, 1911; J. Soc. Chem. Ind. 1911, 412).

1-*p*-Sulphophenyl-3-methyl-5-pyrazolone condenses with diazotised *m*-xylidine-*o*-sulphonic acid forming a yellow dye. Similar compounds are given by the tolyl and carboxyl derivatives of the pyrazolone and by 1-phenyl-3-methyl-5-pyrazolone, all of them being distinguished for their beautiful shade and fastness to light (D. R. P. 176954).

4-Sulphonamino-1-phenyl-2:3-dimethyl-5-pyrazolone is obtained by the action of sodium hydrogen sulphite on 4-nitroso-1-phenyl-2:3-dimethyl-5-pyrazolone, the free acid being subsequently precipitated by hydrochloric acid (D. R. P. 193632).

1-*p*-Dialkylaminophenyl-2:4-dimethyl-3-hydroxymethyl-5-pyrazolones are said to be of therapeutic value, being strong antipyretics. They are produced by alkylating 1-*p*-aminophenyl-2: 4-dimethyl-3-hydroxymethyl-5-pyrazolone with methyl-iodide or sulphate. A number of these substances and their derivatives and similar compounds are described in D. R. PP. 214716; 217557; 217558; *see* also J. Soc. Chem. Ind. 1909, 854.

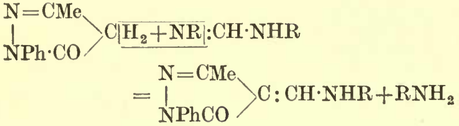
1-*p*-dimethylaminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone, which is used in medicine, may be formed by methylating 1-*p*-aminophenyl-3:4-dimethyl-5-pyrazolone or other suitable pyrazolone or pyrazole derivative. It is said to be less toxic than the corresponding 2:3-dimethyl derivative, but equally active therapeutically (D. R. P. 238256; J. Soc. Chem. Ind. 1911, 1333).

1-Phenyl-2:3-dimethyl-4-isovaleramino-5-pyrazolone and its bromo derivative are described in D. R. PP. 238373; 227013; J. Soc. Chem. Ind. 1911, 49, 1333.

Greenish-yellow dyestuffs fast to light have been obtained by combining the hydrazine of 3-chloro-2-amino-1-methylbenzene-5-sulphonic acid (1 mol.) with oxalyl acetic ester. The resulting pyrazolone is saponified and treated with another molecule of the diazo derivative of the above sulphonic acid (Eng. Pat. 1244, 1909).

When 1-phenyl- or tolyl-2:3-dimethyl-5-pyrazolone and *o*- or *p*-toluene sulphonamide are fused together in molecular proportions, crystalline compounds of therapeutic value are formed (D. R. P. 229814).

Phenylmethyl pyrazolone and the formamidines react smoothly thus

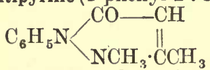


$$\begin{matrix}N{=}CMe\\|\\NPh{\cdot}CO\end{matrix}\!\!>\!C\boxed{H_2+NR}:CH{\cdot}NHR = \begin{matrix}N{=}CMe\\|\\NPhCO\end{matrix}\!\!>\!C:CH{\cdot}NHR+RNH_2$$

forming red or yellow *aminoethylene pyrazolones.* A number of these are described by Dains and Brown (J. Amer. Chem. Soc. 1909, 31, 1148).

Soap-like compounds have been obtained by combining 1 mol. of dimethyl pyrazolone with 2 mols. of higher fatty acids, and dissolving the product in a neutral fat (D. R. P. 171421; J. Soc. Chem. Ind. 1907, 33).

Recent literature on 5-pyrazolone derivatives: Kufferath, J. pr. Chem. 1901, [ii.] 64, 334; Walther and Rothacker, *ibid.* 1906, [ii.] 74, 207; Heiduschka and Rothacker, *ibid.* 1909, [ii.] 80, 289; Curtius and Gockel, *ibid.* 1911, [ii.] 83, 279; Mackerman, *ibid.* 513; *ibid.* 84, 278; Betti, Gazz. chim. ital. 1906, 36, ii. 427: *ibid.* i. 178; Knorr, Ber. 1906, 39, 3265; Bülow and Busse, *ibid.* 2459, 3861; Eibner and Laue, *ibid.* 2022; Michaelis and Schlecht, *ibid.* 1954; Emmerling and Kristeller, *ibid.* 2450; Bülow and Schaub, *ibid.* 1908, 41, 2180; Michaelis and Schenk, *ibid.* 3865; Bülow and Haas, *ibid.* 1910, 43, 2647; Michaelis and Lachwitz, *ibid.* 2106; Benary, *ibid.* 1065; Bülow and Göller, *ibid.* 1911, 44, 2835; Michaelis, Annalen, 1911, 385, 1; Ruhemann, Chem. Soc. Trans. 1907, 1363; Castellana, Atti. R. Accad. Lincei, 1907, [v.] 16, i. 767; Eng. Pats. 9268, 1897; 22391, 1900; 13383, 27485, 1907; Fr. Pats. 362465, 378486, 1907; 398602, 1909; D. R. PP. 233068; 206637; 180120; 189842; 75378; J. Soc. Chem. Ind. 1895, 987; *ibid.* 1897, 160; *ibid.* 1902, 67; *ibid.* 1906, 714; *ibid.* 1907, 1215; *ibid.* 1908, 91, 420; *ibid.* 1909, 328, 832; *ibid.* 1910, 1099.

Antipyrine (1-phenyl-2 : 3-dimethyl-5-pyrazolone)  was discovered by Knorr in 1883, and was introduced into medical use by Filehne. It may be prepared by a variety of methods, thus by heating phenylmethyl pyrazolone with methyl alcohol and methyl iodide (Knorr, Ber. 1884, 17, 549, 2037); by heating 1-phenyl-3-methyl-5-ethoxypyrazole with methyl iodide (D. R. P. 72824; Frdl. 1890–94, iii. 936); by heating the esters of β-halogencrotonic acid with methylphenyl hydrazine (*ibid.* 928; D. R. P. 64444); but is perhaps best manufactured by heating phenyl hydrazine with ethyl acetoacetate. The resulting product is dissolved in methyl alcohol and treated with hydrogen iodide. The addition product thus formed is decomposed with sodium hydroxide, and the antipyrine which separates at first as a heavy oil is recrystallised from toluene or ether (J. Soc. Chem. Ind. 1892, 838). It may also be obtained by the direct action of methylphenyl hydrazine on ethyl acetoacetate. For other methods, *see* D. R. P. 95643; Stolz, J. pr. Chem. [ii.] 55, 148; Michaelis and Pasternack, Ber. 1899, 32, 2406; Frdl. 1894–97, iv. 1192; J. Soc. Chem. Ind. 1891, 656.

Antipyrine forms almost inodorous, mildly bitter, lustrous crystals, m.p. 113°, which, when further heated, turn red, then brown, and acquire an odour resembling amber oil. It has b.p. 141°–142° *in vacuô*, 319°/174 mm. (corr.) (Krafft and Weilandt, Ber. 1895, 29, 2241; Knorr, Annalen, 1896, 293, 1). At 25° it dissolves in less than 1 part of water, in 1 of alcohol or chloroform, and in about 30 of ether.

Tests.—Antipyrine gives a deep red colour with ferric chloride changing to chrome yellow on addition of sulphuric acid (Monferrino, Chem. Zentr. 1909, i. 2029).

Two c.c. of a 1 p.c. solution treated with 2 drops of fuming nitric acid, acquire a green colour which, when boiled and treated with another drop of acid, changes to red, or, if before boiling 5 c.c. of sulphuric acid is added, a cherry-red ring is formed (Sperling, Chem. Zentr. 1906, i. 1118). With nitrous acid it gives a green colouration (Reichard, Chem. Zeit. 1904, 28, 339).

The following reagent gives a very delicate test for antipyrine, 1 grm. vanillin+6 grms. hydrochloric acid diluted with an equal volume of water, +100 grms. 95 p.c. alcohol. Two c.c. of this mixture is poured over a very small crystal of antipyrine and evaporated on the water-bath. A deep orange ring and then a deposit of the same colour is formed; pyramidone does not react thus, and kryogenine gives a yellow-green tint under the same conditions (Primot, Pharm. J. 1909, 83, 9).

For other tests, *see* Jolles, Zeitsch. anal. Chem. 1898, 37, 441; Berenger, Pharm. J. 1904, 72, 117; Steensma, Apoth. Zeit. 1907, 22, 819; Bourcet, Bull. Soc. chim. 1905, [iii.] 33, 572.

Antipyrine may be determined quantitatively thus: A quantity of the sample containing about 0·5 grm. of antipyrine is dissolved in 50 c.c. of water, 5–6 c.c. of N/1 hydrochloric acid is added and the whole heated to boiling. The hot solution is then treated with about 10 c.c. of cold saturated alcoholic picric acid, shaken, and allowed to stand for a few hours, when fine long needles of the picrate separates. The precipitate is collected on a weighed filter, adhering crystals being washed on the filter with the filtrate. They are then drained with a filter pump without washing, and dried at 90°–95° (Riedel, Pharm. J. 1907, 78, 457; *see* also Lemaire, *ibid.* 1905, 74, 13; Schaack, J. Soc Chem. Ind. 1895, 199, 773; Schuyten, *ibid.* 1073; Kippenberger, Zeitsch. anal. Chem. 1896, 35, 659).

Antipyrine is a valuable analgesic. It has been employed successfully in the various forms of nerve pain, and is said to be remarkably efficient in the treatment of migraine, the lancinating pains of locomotor ataxia, in sciatica, and in various neuralgias resulting from nervous depression or antecedent disease. In fevered states it acts as a fairly constant antipyretic. It is also antiseptic, and it has been used in the treatment of various diseases (Sée, Compt. rend. 1887, 105, 103; Jonescu, Chem. Zentr. 1906, i. 1794; Kobert, *ibid.* 1907, i. 1804; Cervello, Arch. exp. Path. Pharm. 1910, 62, 357; *ibid.* 1911, 64, 403).

Antipyrine forms compounds with mercury, zinc, iron, and other metallic salts (Schuyten, Chem. Zentr. 1901, ii. 1362; Eury, *ibid.* 1908, ii. 1037; Garelli and Barbieri, Gazz. chim. ital. 1906, 36, ii. 168; Moulin, Bull. Soc. chim. 1903, [iii.] 29, 201; Astre and Vidal, *ibid.* 1905, 33, 842; *ibid.* 1911, iv. 9, 836, 309; Compt. rend. 1900, 130, 837, 1256; J. Soc. Chem. Ind. 1895, 595).

Ferripyrine $(C_{11}H_{12}N_2O)_3FeCl_3$, prepared by mixing an alcoholic solution of ferric chloride with an alcohol ether solution of antipyrine, forms an orange-red powder which is employed in medicine both internally and externally.

Antipyrine oil (*mercuric iodide antipyrine*) is a bright yellow viscous liquid, sp.gr. 1·3518 at 18°, forming an alkaline aqueous solution and readily soluble in alcohol and in acetone. A white precipitate is formed when treated with sulphuric or hydrochloric acid, or with undistilled water and when boiled with distilled water. It is decomposed when heated and when treated with concentrated sulphuric acid, forming red crystals and liberating iodine. When heated with acetic acid it forms a pale yellow compound, m.p. 133° (Raikow and Külümow, Chem. Zentr. 1905, ii. 1595).

Antipyrine also forms arsenates and phosphates (Aubouy, Bull. Soc. chim. 1908, [iv.] 3, 388), and combines with the halogens and halogen acids (Reychler, *ibid.* 27, 612; Michaelis and Pasternack, *l.c.*; Fichter, J. pr. Chem. 1906, [ii.] 74, 297; Schwabe, Ber. 1900, 33, 2609; Knorr, Annalen, 1887, 238, 216).

Iodoantipyrine is formed by the action of iodochloride on antipyrine, or of iodine on the latter in presence of sodium acetate, and crystallises in colourless glistening needles, m.p. 160° (Bougault, Chem. Zentr. 1900, i. 507). It combines the properties of iodine and of an antipyretic.

Nitro- and amino-antipyrines are described by Michaelis (Annalen, 1911, 378, 293).

The most important amino derivative is the 4-*dimethyl amino-antipyrine* or *pyramidone*, which has a similar physiological action to antipyrine, but has a more powerful and lasting effect on the nervous system than the latter.

Dimethyl- and diethyl-aminoantipyrine is obtained by heating aminoantipyrine hydrochloride with chloro- or bromoacetic or propionic acid and sodium carbonate. The product is then treated with 10 p.c. sulphuric acid and subsequently with caustic soda (Eng. Pat. 26353, 1902; J. Soc. Chem. Ind. 1904, 35).

Pyramidone is also formed by reducing an acetic acid solution of *iso*nitrosoantipyrine, the amino antipyrine formed is then treated with methyl chloride or iodine (Kollo, Pharm. J. 1911, 86, 711); or by methylating acyl or alkyl derivatives of 4-amino-1-phenyl-3-methyl-5-pyrazolone, the acyl or alkyl group attached to a nitrogen or pyrazolone oxygen atom, being readily eliminated (D. R. P. 189842). Pyramidone is an almost tasteless, yellowish-white, crystalline powder, m.p. 108°, soluble in 10 parts of water. It may be distinguished from antipyrine by the fugitive violet-blue colour formed when either ferric chloride, nitrous or fuming nitric acid is added (Monferrino, Chem. Zentr. 1909, i. 2029; for other tests, *see* Moulin, Ann. Chim. anal. 1911, 16, 220; J. Soc. Chem. Ind. 1900, 778; Kollo, *l.c.*; also tests for antipyrine). For certain microchemical reactions of pyramidone, *see* J. Soc. Chem. Ind. 1906, 1171).

Pyramidone may be estimated by treating its solution with a measured excess of picric acid, then titrating the excess of the latter with caustic soda (Astruc and Pégurier, Chem. Zentr. 1905, ii. 927, 1554; *see* also Lemaire, Ann. Chim. anal. 1910, 15, 307).

Acetanilide is sometimes found as an impurity both in antipyrine and in pyramidone, and may readily be detected by the abnormal melting-point of the mixtures (Saporetti, Boll. Chim. Farm. 1909, 48, 367).

Pyramidone hydrochloride has m.p. 143°–144°, the *hydrobromide* has m.p. 170°–171° (Astre and Aubouy, Bull. Soc. chim. 1906, [iii.] 35, 856).

Hydriodic acid acts on pyramidone forming the *hydriodide* $C_{13}H_{17}ON_3,HI$, colourless prisms, m.p. above 200° (decomp.). When iodine is added to the latter, the *periodide*

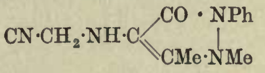
$$C_{13}H_{17}ON_3,HI,I_2$$

is formed as brown insoluble needles (Cousin, J. Pharm. Chim. 1909, [vi.] 29, 49).

Pyramidone reacts with Nessler's reagent forming a sulphur yellow crystalline mercuric iodide compound, m.p. 170°–172° (Raikow and Külümow, *l.c.*).

The secondary *citrate* of 1-*phenyl*-2 : 3-*dimethyl*-4-*dimethylamino*-5-*pyrazolone*, m.p. 85°, is formed by heating 1 mol. of citric acid with 2 mols. of the pyrazolone (D. R. P. 234631; J. Soc. Chem. Ind. 1911, 833).

4-Antipyrylcyanomethylamine



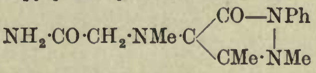
$$\mathrm{CN{\cdot}CH_2{\cdot}NH{\cdot}C}\left\langle\begin{array}{l}\mathrm{CO\cdot NPh}\\ \qquad\quad|\\ \mathrm{CMe{\cdot}NMe}\end{array}\right.$$

colourless leaflets, m.p. 112°, is formed by treating 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone successively with formaldehyde, sodium hydrogen sulphite and potassium cyanide.

4-Antipyrylaminoacetamide, colourless prisms, m.p. 194°, is obtained by boiling the above methylamine with water or leaving it in contact with concentrated hydrochloric acid. When boiled with the latter it forms a betaine, m.p. above 300°.

4-Antipyrylcyanodimethylamine, colourless crystals, m.p. 75°, is prepared by alkylating the monomethylamine.

4-Antipyrylmethylaminoacetamide



$$\mathrm{NH_2{\cdot}CO{\cdot}CH_2{\cdot}NMe{\cdot}C}\left\langle\begin{array}{l}\mathrm{CO{-}NPh}\\ \qquad\quad|\\ \mathrm{CMe{\cdot}NMe}\end{array}\right.$$

m.p. 158°–159°, is obtained by methylating the above aminoacetamide, whilst 4-*antipyrylmethylaminoacetic acid* is similarly prepared from the above betaine. The last three compounds when hydrolysed yield the therapeutically valuable pyramidone (D. R. P. 184850; J. Soc. Chem. Ind. 1907, 947).

Dimethylaminoazoantipyrine, brownish-yellow leaflets, m.p. 107° (rapid heating), 110°–112° (slow heating), may be prepared by coupling dimethylamine with diazoantipyrine. When heated to 130°–140° it yields 1-phenyl-2-methyl-3 : 4-pyrazopyrazol-5-one, orange crystals, m.p. 173°. The corresponding diethyl azoantipyrine forms light brown prisms, m.p. 111°–112° (Stolz, Ber. 1908, 41, 3849).

Antipyrine salicylate (*salipyrine*)

$$C_{11}H_{12}N_2O,C_7H_6O_3,$$

formed by fusing together the constituents, is a crystalline powder, m.p. 92°, which is employed as an antiseptic and preservative. Its dimethyl derivative may be formed similarly (Eng. Pats. 10432, 1890; 11040, 1900; J. Soc. Chem. Ind. 1891, 655; *ibid.* 1901, 504; *ibid.* 1902, 272).

Antipyrine mandelate (*Tussol*)

$$C_{11}H_{12}N_2O,C_8H_8O_3,$$

formed by mixing solutions of the constituents, is a white crystalline powder, m.p. 53° (Eng. Pat. 11774, 1894; J. Soc. Chem. Ind. 1895, 595).

Antipyrine-β-resorcylate, obtained by the combination of 2 mols. of base and 1 of the acid, forms colourless acid crystals, m.p. 115° (Petit and Févre, Chem. Zeit. 1894, 18, 1094).

Antipyrine valerate, has an unpleasant taste, but is more energetic physiologically than antipyrine (Sochaczewski, J. Soc. Chem. Ind. 1891, 159).

Formopyrine (*Methylene diantipyrine*)

$$(C_{11}H_{12}N_2O)_2CH_2,H_2O,$$

prepared by the interaction of antipyrine and formaldehyde, has m.p. 155°–165°, anhydrous, 177°.

Chloral antipyrine (*Hypnal*)

$$C_{11}H_{12}N_2O,CCl_3{\cdot}CH(OH)_2,$$

formed by the interaction of the constituents, has m.p. 67°–68°. If the temperature is raised to 100°–110°, it forms the compound

$$C_{11}H_{12}N_2O,CCl_3{\cdot}CHO,$$

m.p. 186°–187°. A dichloral also, m.p. 67°–68°, but more soluble than the mono-, is known (Behal and Choay, Ann. Chim. Phys. 1892, [vi.] 27, 330; Patein, Compt. rend. 1897, 125, 956).

Butylchloralantipyrine, formed like hypnal, has m.p. 70° (Calderato, Chem. Zentr. 1902, ii. 1387).

Ethoxyantipyrine $C_{11}H_{11}(OEt)N_2O$ is prepared like antipyrine, ethoxyphenyl hydrazine being used. It has m.p. 91° (Eng. Pats. 2617, 1892; 14716, 1892; J. Soc. Chem. Ind. 1893, 288, 784).

Migraenine is a compound containing 90 parts of antipyrine, 9 of caffeine, and 1 of citric acid (Sleeswijk, Chem. Zentr. 1911, i. 268).

Antipyrine urethane acetamide, m.p. 181°, is described by Lumière and Barbier (Bull. Soc. chim. 1906, [iii.] 35, 123). Antipyrine compounds of piperazine, piperidine, and morpholine have been described by Luft (Ber. 1905, 38, 4044), of camphor sulphonate by Reychler (J. Soc. Chem. Ind. 1902, 987), of saccharin in D. R. P. 131741; Chem. Zentr. 1902, i. 1287. Soluble antipyrine compounds of alkyl glycollic, butyric, and valeric acids are described in D. R. P. 218478. Antipyrine methyl ethyl glycollate, *v.* ASTROLIN; Winzheimer, Pharm. Zeit. 1909, 54, 660.

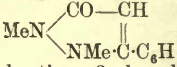
For a number of other compounds of antipyrine, *see* Patein and Dufan, Bull. Soc. chim. [iii.] 15, 172, 609, 849, 1049; Einhorn and Ruppert, Annalen, 1902, 325, 318; D. R. P. 126340.

Tolylpyrine $C_{12}H_{14}N_2O$ is prepared like antipyrine from *p*-tolylhydrazine. It forms colourless, bitter crystals, m.p. 136°–137°, soluble in 14 parts of water at 15° (Knorr, Ber. 1884, 17, 549; Michaelis and Sudendorf, *ibid.* 1900, 33, 2617).

Tolylpyrine salicylate (*Tolysal*), m.p. 100°–101°, is employed in the treatment of nervous derangement and neuralgic pains (Eng. Pat. 19329, 1892; J. Soc. Chem. Ind. 1893, 546). A number of derivatives of tolylpyrine are described by Ebert (Pharm. Zeit. 1893, 38, 251; *see* also Einhorn and Ruppert, *l.c.*; Coblentz, J. Soc. Chem. Ind. 1898, 727).

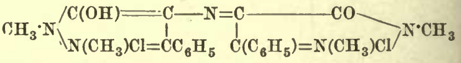
Homoantipyrine (1-Ph-3-Me-2-ethyl pyrazolone). Sulphides of this and of antipyrine are described by Konek and Norwall (7th Intern. Congr. Appl. Chem. 1909, sect. iv., AI. 234). The corresponding tolyl compound is described in D. R. P. 92009; Frdl. 1894–97, iv. 1198.

*iso***Antipyrine**



$$\mathrm{MeN}\left\langle\begin{array}{l}\mathrm{CO{-}CH}\\ \qquad\ \ \|\\ \mathrm{NMe{\cdot}C{\cdot}C_6H_5}\end{array}\right.$$

, m.p. 108° is formed by heating 3-phenyl-1-methyl-5-pyrazolone (m.p. 207)° with methyl iodide in a sealed tube at 100° (Michaelis, Annalen, 1907, 352, 152, 175). The corresponding *iso*amino-antipyrine, when oxidised with ferric chloride, yields a soluble dyestuff termed iso*antipyrine red* (the methyl chloride of *iso*rubazonic acid), m.p. 207°

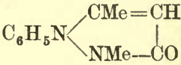


$$\mathrm{CH_3{\cdot}N}\left\langle\begin{array}{llll}\mathrm{C(OH){=}} & \mathrm{C{-}N{=}} & \mathrm{C{-}} & \mathrm{CO}\\ & \ \, | & \, | & \\ \mathrm{N(CH_3)Cl{=}} & \mathrm{CC_6H_5} & \mathrm{C(C_6H_5){=}} & \mathrm{N(CH_3)Cl}\end{array}\right\rangle\mathrm{N{\cdot}CH_3}$$

With alkalis it forms a diantipyrylamine. A corresponding antipyrine red is formed by oxidising aminoantipyrine with ferric chloride. It has m.p. 215°, and behaves like the *iso-* compound with alkalis and reducing agents (Michaelis, *ibid.* 213).

*iso***Pyramidone** is best obtained by the action of dimethyl sulphate on amino*iso*antipyrine. It has m.p. 118°, and is less poisonous than ordinary pyramidone (*ibid.* 209). A large number of derivatives of *iso*antipyrine and of *iso*-pyramidones are described in the same paper.

3-Antipyrine



$$\mathrm{C_6H_5N}\left\langle\begin{array}{l}\mathrm{CMe{=}CH}\\ \qquad\quad\ |\\ \mathrm{NMe{-}CO}\end{array}\right.$$

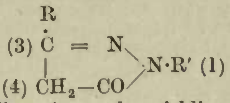
, m.p. 113°, is formed by treating the corresponding phenyl methyl pyrazolone with methyl alcohol and methyl iodide. It is a powerful antipyretic, and resembles antipyrine very closely, but some of its derivatives have different melting-points (D. R. P. 53834; Lederer, J. pr. Chem. 1892, [ii.] 45, 83; *see* Michaelis, *l.c.*). The corresponding 3-*pyramidone* has m.p. 74°. Derivatives of 3-antipyrine are described by Michaelis (*ibid.* 1907, 358, 127).

Thio-pyrazolones, thio-antipyrines, or **thiopyrines,** in which the oxygen atom is replaced by sulphur have been obtained by the action of potassium hydrogen sulphide on the methochloride or iodide of the required halogen pyrazole (Michaelis and Bindewald, Annalen, 1901, 320, 1; Ber. 1900, 33, 2873); or by the action of phosphorus pentasulphide on the pyrazolones (Stoermer and Johannsen, *ibid.* 1907, 40, 3701).

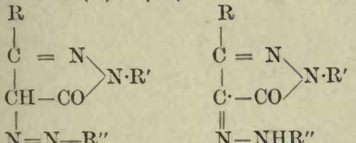
Like the pyrazolones, thio-pyrazolones condense with benzaldehyde and with ketones in molecular proportions, form coloured azo compounds, and have both acid and basic properties, the former being more strongly pronounced in the thio derivatives. The latter differ from pyrazolones in yielding ψ-, not normal alkyl thiopyrines with alkyl iodides, unstable nitroso-compounds, which rapidly change into disulphides, and azo ψ-thiopyrines (not normal). On oxidation they do not form bis- compounds, but disulphides or sulphonic acids, and on further oxidation they yield colourless compounds in which two thiopyrazolone groups are united by a sulphur and a carbon linking, and which are, therefore, wholly unlike the constitution of pyrazole blue (Michaelis, Annalen, 1908, 361, 251; *see* also *ibid.* 1907, 352, 187; *ibid.* 354, 55; *ibid.* 358, 127; *ibid.* 1911, 378, 293).

Similar *seleno* derivatives have also been obtained.

PYRAZOLONE COLOURING MATTERS. Derivatives of pyrazolone, which have substituting groups in the positions 1 and 3, and which are therefore constituted in accordance with the general formula

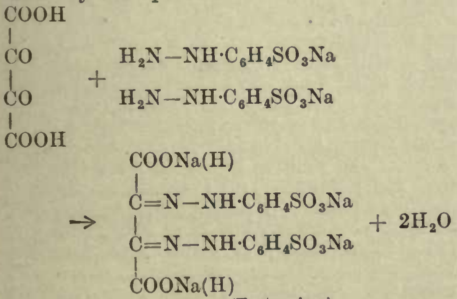


react with diazonium salts yielding azo compounds having the azo residue in the position 4. These compounds are colouring matters and possess a constitution which is represented by either formula (I.) or (II.)—



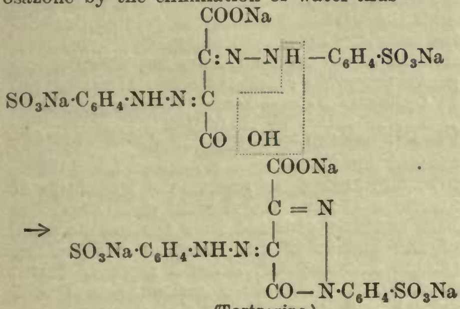
(Azo form.) (Hydrazone form.)

The only colouring matter of this series which is, at present, of importance is *Tartrazine*, a compound which was prepared by Ziegler (Ber. 1887, 20, 834) by the interaction of phenylhydrazine sulphonic acid and sodium dihydroxytartrate. It is evident that in this reaction, dihydroxytartaric acid behaves as a di-ketone and it was concluded that tartrazine had the hydrazone formula, the reaction being represented by the equation



(Tartrazine.)

Anschutz (Annalen, 1897, 294, 226; 1899, 306, 1; *cf.* also Gnehm and Benda, *ibid.* 1898, 299, 127) has shown, however, that this sulphonic acid is only an intermediate product in the formation of tartrazine and that the dye is formed from the osazone by the elimination of water thus—



(Tartrazine.)

Tartrazine is therefore the sodium salt of di-*p*-sulphophenylhydrazonopyrazolonecarboxylic acid.

Preparation. 10 grms. of phenylhydrazine sulphonic acid, 5 grms. of sodium dihydroxytartrate and 35 c.c. of water are mixed together in a mortar and then warmed in a flask, placed on the water-bath, until complete solution is effected. The liquid is then boiled until it ceases to become darker in colour, when it is neutralised by the addition of concentrated aqueous sodium carbonate, filtered while hot, and allowed to crystallise. If the colour does not separate readily, salt must be added to the solution.

Properties. Tartrazine, in the form of the trisodium salt, is used as an acid dye for wool. It is a yellow crystalline powder readily soluble in water.

Reactions. Alcohol precipitates the colour from its aqueous solution; stannous chloride gives a yellow precipitate soluble in oxalic acid. The addition of caustic soda causes the aqueous solution to become darker. J. F. T.

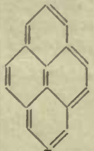
PYRENE $C_{16}H_{10}$ occurs with chrysene and other high boiling-point hydrocarbons in the final fraction obtained in the distillation of coal-tar (Graebe, Annalen, 1871, 158, 285); it is also found mixed with fluoranthrene in the so-called 'stupp-fat,' which was obtained as a by-product in the old Idrian process of distilling mercury ores.

Extraction.—(1) From coal tar. The pyrene fraction is treated with carbon disulphide, which dissolves the pyrene and leaves the chrysene and other hydrocarbons. The solution is evaporated and the impure pyrene dissolved in alcohol; on adding an alcoholic solution of picric acid a characteristic insoluble picrate separates out. When this is treated with ammonia, pyrene is liberated and may be obtained pure by recrystallisation from alcohol.

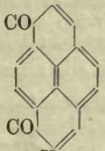
(2) From stupp-fat. The more soluble impurities are first removed with cold alcohol; the residue is dissolved in boiling alcohol, and the insoluble picrate is prepared as above.

Properties and reactions. Pyrene forms monoclinic tables melting at 149°; it boils at a temperature higher than 360°. It is moderately soluble in alcohol, considerably more so in toluene, ether, and carbon disulphide. On oxidation with chromic anhydride, pyrenequinone and then pyrenic acid are formed; on reduction hexahydro-pyrene is obtained; on chlorination, mono-, di-, tri-, and tetra- chloro derivatives; on nitration mono-, di-, and tetranitro derivatives; on sulphonation a disulphonic acid are obtained.

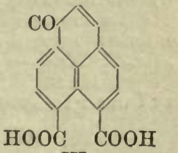
Constitution. Bamberger and Philip (Annalen, 1890, 240, 158) regarded pyrene as containing the naphthalene nucleus to which two benzene nuclei were joined in the peri positions. According to Goldschmidt (Chem. Zentr. 1907, [i.] 1421), and Langstein (*ibid.* 1910, [ii.] 1760), the arrangement of the linkings in the molecule is different, pyrene (I.), pyrene quinone (II.), and pyrenic acid (III.) having the constitutions given below—



I.



II.



III.

Pyrene is also closely related to thebenol, from which it is obtained by reduction with zinc dust (Freund, Ber. 1897, 30, 1357, 1374).

PYRENOL, PYROSAL *v.* SYNTHETIC DRUGS.

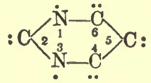
PYRETHRIC ACID *v.* RESINS.

PYRETHRIN *v. Pellitory resin,* art. RESINS.

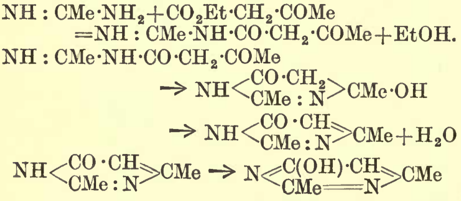
PYRETOL. The active principle of 'insect powder' (Pyrethrum flowers). An odourless, non-volatile light yellow resinoid substance extremely toxic to cold-blooded animals.

PYRIDINE DERIVATIVES, DYESTUFFS, and **HOMOLOGUES** *v.* BONE OIL.

PYRIMIDINES or **METADIAZINES** are compounds containing the heterocyclic ring

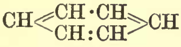


The earliest known members of the series were termed *cyanalkines,* because they were obtained by the polymerisation of alkyl nitriles by the action of sodium or sodium ethoxide. *Cyanethine* was discovered by Kolbe and Frankland (Annalen, 1848, 68, 269). E. v. Meyer (Ber. 1871, 4, 176; J. pr. Chem. 1883, [ii.] 27, 152; 1889, [ii.] 39, 156; [ii.] 40, 303) prepared the lower homologue *cyanmethine,* and showed that it was a metadiazine, *aminodimethylmetadiazine* $\mathrm{MeC}{<}\substack{\mathrm{N:CMe{—}}\\ \mathrm{N\cdot C(NH_2)}}{>}\mathrm{CH}$, and that the hydroxy derivative obtained by the action of nitrous acid (Wollner, *ibid.* 1884, [ii.] 29, 131), *hydroxydimethylmetadiazine,* is identical with the *dimethylhydroxypyrimidine* obtained by Pinner (Ber. 1884, 17, 2519; 1885, 18, 759, 2848; 1887, 20, 2361; 1889, 22, 1612) by the condensation of ethyl acetoacetate and acetamidine



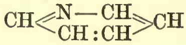
$$\mathrm{NH:CMe\cdot NH_2+CO_2Et\cdot CH_2\cdot COMe}$$
$$\mathrm{=NH:CMe\cdot NH\cdot CO\cdot CH_2\cdot COMe+EtOH.}$$
$$\mathrm{NH:CMe\cdot NH\cdot CO\cdot CH_2\cdot COMe}$$
$$\rightarrow \mathrm{NH}{<}\substack{\mathrm{CO\cdot CH_2}\\ \mathrm{CMe:N}}{>}\mathrm{CMe\cdot OH}$$
$$\rightarrow \mathrm{NH}{<}\substack{\mathrm{CO\cdot CH}\\ \mathrm{CMe:N}}{>}\mathrm{CMe+H_2O}$$
$$\mathrm{NH}{<}\substack{\mathrm{CO\cdot CH}\\ \mathrm{CMe:N}}{>}\mathrm{CMe} \rightarrow \mathrm{N}{<}\substack{\mathrm{C(OH)\cdot CH}\\ \mathrm{CMe{=\!=}N}}{>}\mathrm{CMe}$$

Pinner gave the name *pyrimidine* to the then hypothetical first member of the series, because it stands in the same relation to pyridine as does pyridine to benzene:—



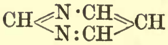
$$\mathrm{CH}{<}\substack{\mathrm{CH\cdot CH}\\ \mathrm{CH:CH}}{>}\mathrm{CH}$$

Benzene.



$$\mathrm{CH}{<}\substack{\mathrm{N{—}CH}\\ \mathrm{CH:CH}}{>}\mathrm{CH}$$

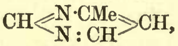
Pyridine.



$$\mathrm{CH}{<}\substack{\mathrm{N\cdot CH}\\ \mathrm{N:CH}}{>}\mathrm{CH}$$

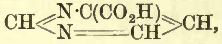
Pyrimidine.

Pyrimidine $\mathrm{C_4H_4N_2}$ was obtained by Gabriel and Colman (Ber. 1899, 32, 1525) from methyluracil (4-*methyl*-2 : 6-*dioxytetrahydropyrimidine*) by the following series of reactions: methyluracil is converted by the action of phosphoryl chloride into 4-*methyl*-2 : 6-*dichloropyrimidine* $\mathrm{ClC}{<}\substack{\mathrm{N\cdot CMe}\\ \mathrm{N:CCl}}{>}\mathrm{CH}$, this is reduced by zinc-dust and water to 4-*methylpyrimidine*



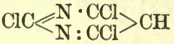
$$\mathrm{CH}{<}\substack{\mathrm{N\cdot CMe}\\ \mathrm{N:CH}}{>}\mathrm{CH},$$

which, on oxidation with potassium permanganate, yields *pyrimidine-4-carboxylic acid*



$$\mathrm{CH}{<}\substack{\mathrm{N\cdot C(CO_2H)}\\ \mathrm{N{=\!=\!=}CH}}{>}\mathrm{CH},$$

from which *pyrimidine* $\mathrm{CH}{<}\substack{\mathrm{N\cdot CH}\\ \mathrm{N:CH}}{>}\mathrm{CH}$ is obtained by distillation. Pyrimidine is more conveniently obtained by reducing with zinc-dust the 2 : 4 : 6-*trichloropyrimidine*



$$\mathrm{ClC}{<}\substack{\mathrm{N\cdot CCl}\\ \mathrm{N:CCl}}{>}\mathrm{CH}$$

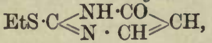
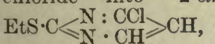
obtained by the action of phosphoryl chloride on barbituric acid (2 : 4 : 6-*trioxyhexahydropyrimidine*) (Gabriel, Ber. 1900, 33, 3666; Gabriel and Colman, *ibid.* 1904, 37, 3657); or by similarly reducing 2 : 4 : 5 : 6-tetrachloropyrimidine obtained from alloxan (2 : 4 : 5 : 6-*tetraoxyhexahydropyrimidine*) (Ciamician and Magnaghi, *ibid.* 1885, 18, 3444), or from dialuric acid (2 : 4 : 6-*trioxy-5-hydroxyhexahydropyrimidine*) (Emery, *ibid.* 1901, 34, 4178). Pyrimidine is a crystalline compound with a penetrating, stupefying odour, it has m.p. 20°–22°, b.p. 123·5°–124°/762 mm.; it is soluble in water, forming a solution neutral to litmus; the *mercurichloride* and *aurichloride* are crystalline, the latter melts at 226°; the *picrate* forms pale yellow needles, and has m.p. 156°. 2 : 4 : 6-*Trichloropyrimidine* has m.p. 21°, and b.p. 213°/755 mm. (Gabriel, Ber. 1900, 33, 3666); 2 : 4 : 5 : 6-*tetrachloropyrimidine* has m.p. 70°, yields *trichloroiodopyrimidine,* m.p. 93°–94°, and *dichlorodiiodopyrimidine,* m.p. 159°, by the action of sodium iodide; 2 : 4 : 5 : 6-*tetrabromopyrimidine* has m.p. 165°–166° (Emery, *l.c.*).

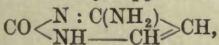
2 : 4 : 6-*Triaminopyrimidine,* m.p. 245°–246°, obtained by the action of alcoholic ammonia on the trichloro compound forms crystalline salts, and is converted by fuming nitric and sulphuric acids into 5-*nitro*-2 : 4 : 6-*triaminopyrimidine,* which on reduction yields 2:4:5:6-*tetraaminopyrimidine,* orange-yellow prisms, with no definite melting-point, forming a strongly alkaline solution in water and yielding crystalline salts (Gabriel, Ber. 1901, 34, 3362); 2 : 4-*dichloro-5-nitropyrimidine,* obtained by heating 5-nitrouracil with phosphoryl chloride, has m.p. 29·3°, and b.p. 153°–155°/58 mm.; it yields with ammonia 2-*chloro*-5-*nitro*-4-*amino-pyrimidine,* m.p. 217°, which can be reduced to 4 : 5-*diaminopyrimidine,* m.p. 202·5°, b.p. 229°/32 mm. (Isay, *ibid.* 1906, 39, 250).

A very large number of pyrimidine derivatives have been prepared, and the chemistry of the group covers a wide field, much of it lying beyond the scope of this present article. Certain of the pyrimidines, *cytosine, thymine,* and *uracil,* occur among the degradation products of the proteins; others, including the alkyl derivatives of barbituric acid, have important therapeutic properties; and these merit description.

Cytosine, 2-*oxy*-6-*aminodihydropyrimidine* $\mathrm{C_4H_5N_3O_3,H_2O}$; $\mathrm{CO}{<}\substack{\mathrm{N:C(NH_2)}\\ \mathrm{NH{—\!—}CH}}{\geqslant}\mathrm{CH}$, was discovered by Kossel and Neumann (Ber. 1894, 27, 2215) among the products of hydrolysis of nucleic acid from the thyroid gland, and has been similarly obtained from the nucleic acids of the testicle of the sturgeon and herring (Kossel and Steudel, Zeitsch. physiol. Chem. 1902, 37, 177), and other nucleic acids of both animal and vegetable origin (Inouye, *ibid.* 1905, 46, 201; Mandel and Levene, *ibid.* 1905, 46, 155; 1906, 47, 140; 49, 262; 50, 1; Kossel and Steudel, *ibid.* 1903, 38, 49; Osborne and Heyl, Amer. J. Physiol. 1908, 21, 157; Wheeler and Johnson, Amer. Chem. J. 1903, 29, 505; Schreiner and Lathrop, J. Amer. Chem. Soc. 1912, 34, 1242).

The question has been raised by Burian (Zeitsch. physiol. Chem. 1907, 51, 438), and by Osborne and Heyl (Amer. J. Physiol. 1908, 21, 157), whether the pyrimidine bases from nucleic acid are primary products of hydrolysis or arise from the purine bases by a process of hydrolysis and reduction. The results obtained by Levene and Jacobs, and La Forge (Ber. 1910, 43, 3150; 1911, 44, 1027; 1912, 45, 608), serve to show that these bases are primary products of hydrolysis, for the authors have isolated the pyrimidine nucleotides, *cytidine nucleotide* $PO(OH)_2{\cdot}O{\cdot}C_9H_{12}O_4N_3$ and *uridine nucleotide* $PO(OH)_2{\cdot}O{\cdot}C_9H_{11}O_5N_2$ by the partial hydrolysis of yeast nucleic acid, and shown that cytidine is a complex containing one molecule of cytosine and one of ribose. *Cytidine* crystallises in long needles, m.p. 230° (decomposition), it has $[\alpha]_D^{21}+29{\cdot}63°$, and forms a sparingly soluble *nitrate;* the *picrate* has m.p. 185°–187°, the *sulphate* m.p. 233°, and the *hydrochloride* m.p. 218°, and the *tribenzoyl* derivative has m.p. 205°.

Cytosine has been prepared synthetically by Wheeler and Johnson (Amer. Chem. J. 1903, 29, 492, 505) by the following series of reactions: ψ-ethylthiocarbamide hydriodide and ethyl sodioformylacetate condense to form 2-*ethylthiol*-6-*oxydihydropyrimidine*  $\mathrm{EtS{\cdot}C}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{N\cdot CH}\end{matrix}>\mathrm{CH}$, converted by the action of phosphorus pentachloride into 2-*ethylthiol*-6-*chloropyrimidine*  $\mathrm{EtS{\cdot}C}<\begin{matrix}\mathrm{N:CCl}\\ \mathrm{N\cdot CH}\end{matrix}>\mathrm{CH}$, this reacts with alcoholic ammonia to form the 6-*amino* derivative, which yields, on prolonged boiling with hydrobromic acid, 2-*oxy*-6-*aminodihydropyrimidine*



$$\mathrm{CO}<\begin{matrix}\mathrm{N:C(NH_2)}\\ \mathrm{NH{-\!-}CH}\end{matrix}>\mathrm{CH},$$

identical with the natural cytosine.

Cytosine crystallises with one molecule of water in thin colourless pearly plates, becomes anhydrous at 100°, blackens at 300°, and decomposes at 320°–325°; it is insoluble in ether, sparingly soluble in alcohol or water, 1 part dissolving in 129 parts of water at 25°.

Cytosine is readily converted into uracil (2 : 6-dioxytetrahydropyrimidine) by the action of nitrous acid, or partially by heating with 20 p.c. sulphuric acid at 150°–170°. Both cytosine and uracil give a characteristic purple colour when dissolved in bromine water, and the solution treated with barium hydroxide solution; the dibromohydroxyhydrouracil first formed is converted by the barium hydroxide into *iso*-dialuric acid, which immediately undergoes a rearrangement in the alkaline solution to give the purple barium salt of dialuric acid (Wheeler and Johnson, J. Biol. Chem. 1907, 3, 183). Cytosine, thymine or uracil gives with diazobenzenesulphonic acid a red solution in the presence of alkali, the colour given by thymine being the most intense (Johnson and Clapp, J. Biol. Chem. 1908, 5, 163).

Salts.—Cytosine forms crystalline salts with acids, and compounds with certain metallic salts (Kossel and Steudel, Zeitsch, physiol. Chem. 1903, 38, 49; Kutscher, *ibid.* 170; Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111; Wheeler and Johnson, Amer. Chem. J. 1904, 31, 591, 605); the *hydrochloride*

$$C_4H_5N_3O,HCl,H_2O,$$

forms large plates that become anhydrous at 50°, and melt at 275°–279°; the *acid salt*

$$C_4H_5N_3O,2HCl$$

forms flat prisms; the *hydrobromide*

$$C_4H_5N_3O{\cdot}HBr,$$

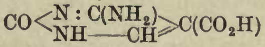
shining prisms; *nitrate* $C_4H_5N_3O{\cdot}HNO_3$; *basic sulphate* $(C_4H_5N_3O)_4H_2SO_4,2H_2O$, sparingly soluble needles, decomposes at 323°; *normal sulphate* $(C_4H_5N_3O)_2{\cdot}H_2SO_4,2H_2O$, prisms, m.p. 287°; *acid sulphate* $C_4H_5N_3O{\cdot}H_2SO_4$, rhombic crystals, m.p. 197°; *phosphate* $C_4H_5N_3O{\cdot}H_3PO_4$, prisms, m.p. 236°; the *silver nitrate compound* $C_4H_5N_3O{\cdot}AgNO_3$ forms needles; *platinichloride* $(C_4H_5N_3O{\cdot}HCl)_2PtCl_4$, sparingly soluble yellow crystals; *picrate* $C_4H_5N_3O{\cdot}C_6H_3N_3O_7$, yellow shining needles, m.p. 270° (Kossel and Steudel), 300°–305° (Wheeler and Johnson); the *picrolonate* $C_4H_5N_3O,C_{10}H_8N_4O_5$ forms fine needles or prisms, m.p. 270°–273°.

Substituted derivatives.—4-*Chlorocytosine*

$$\mathrm{CO}<\begin{matrix}\mathrm{N:C(NH_2)}\\ \mathrm{NH{-\!-}CCl}\end{matrix}>\mathrm{CH},$$

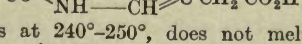
forms small needles, does not melt at 300° (Wheeler and Jamieson, Amer. Chem. J. 1904, 32, 342); 5-*bromocytosine* $C_4H_4ON_3Br$ decomposes at 235° (Wheeler and Johnson, *ibid.* 1904, 31, 591); 5-*iodocytosine* $C_4H_4ON_3I$ decomposes between 225° and 245° (Johnson and Johns, J. Biol. Chem. 1906, 1, 305). The *picrate* $C_4H_4ON_3I{\cdot}C_6H_3O_7N_3$ decomposes at 247°–257°; 5-*nitrocytosine* $C_4H_4N_3O{\cdot}NO_2$, formed by direct nitration of cytosine, crystallises in colourless needles, decomposes at 300°; the *hydrochloride* $C_4H_4O_3N_4,HCl$ does not decompose below 300°; on reduction the nitro derivative yields 5-*aminocytosine* (5 : 6-diamino-6-oxydihydropyrimidine) $C_4H_4ON_3(NH_2),H_2O$, this loses H_2O at 120°–130°, and decomposes above 230° (Johnson, Johns and Heyl, Amer. Chem. J. 1906, 36, 160). 2-*Oxy*-6-*acetaminodihydropyrimidine*, obtained by heating cytosine with acetic anhydride, does not melt at 300° (Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492).

Cytosine-5-*carboxylic acid*



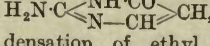
$$\mathrm{CO}<\begin{matrix}\mathrm{N:C(NH_2)}\\ \mathrm{NH{-\!-}CH}\end{matrix}>\mathrm{C(CO_2H)}$$

decomposes at 256°–257°, the *amide* does not melt at 310°, the *hydrochloride, nitrate, sulphate,* and *picrate* are crystalline (Wheeler and Johns, Amer. Chem. J. 1907, 38, 594; 1908, 40, 233), *Cytosine*-5-*acetic acid*

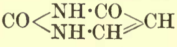


$$\mathrm{CO}<\begin{matrix}\mathrm{N:C(NH_2)}\\ \mathrm{NH{-\!-}CH}\end{matrix}>\mathrm{C{\cdot}CH_2{\cdot}CO_2H}$$

blackens at 240°–250°, does not melt below 290°, the *picrate* has m.p. 217°–218° (Johnson, Peck and Ambler, J. Amer. Chem. Soc. 1911, 33, 758).

iso-*Cytosine*, 2-*amino*-6-*oxydihydropyrimidine*  $\mathrm{H_2N{\cdot}C}<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{N{-\!-}CH}\end{matrix}>\mathrm{CH}$, prepared by the condensation of ethyl sodioformylacetate with guanidine, crystallises from water in thick prisms, melts at 276° with decomposition (Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492); for the *salts* and *derivatives, see* Wheeler and Johnson, Amer. Chem. J. 1903, 29, 492; 1904, 31, 591; Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111.

Uracil, 2 : 6-*dioxytetrahydropyrimidine*



$$\mathrm{CO}\Big<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}\Big\geqslant\mathrm{CH}$$

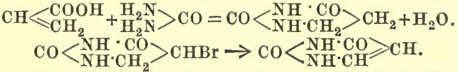
was first obtained, together with thymine and cytosine, by the hydrolysis of yeast nucleic acid (Ascoli, Zeitsch. physiol. Chem. 1900, 31, 161), and is similarly formed from other nucleic acids (Kossel and Steudel, *ibid.* 1902, 37, 245; Levene, *ibid.* 1903, 39, 4; Levene and Strokey, *ibid.* 1904, 41, 404); it is also obtained on autolysis of pancreas (Levene, *ibid.* 1903, 37, 527; Reh, Beitr. chem. Physiol. Path. 1903, 3, 569; Jones, Zeitsch. physiol. Chem. 1904, 42, 35; Levene and Mandel, *ibid.* 1906, 49, 262); and forms one of the bases not precipitated by ammoniacal silver nitrate from secale extract (Engeland and Kutscher, Centralbl. Physiol. 1910, 24, 589).

By the partial hydrolysis of yeast nucleic acid, Levene, Jacobs and La Forge (Ber. 1910, 43, 3150; 1911, 44, 1027; 1912, 45, 608) have obtained the *uridine nucleotide*

$$\mathrm{P(OH)_2\cdot O\cdot C_9H_{11}O_5N_2},$$

from which the nucleoside *uridine* $C_9H_{12}O_6N_2$ can be prepared by hydrolysis with ammonia; it can also be obtained by the action of nitrous acid on cytidine. *Uridine* is a complex containing uracil and ribose in molecular proportion, it crystallises in long prismatic needles, m.p. 165°, and has $[\alpha]_D^{30}+5{\cdot}15°$, $[\alpha]_D^{20}+6{\cdot}40°$; 5-*bromouridine* has m.p. 181°–184°, $[\alpha]_D^{21}-15{\cdot}4°$; *hydroxyuridine* has m.p. 222°–223°, the *phenylhydrazide* has m.p. 209°; *dihydrouridine* is a colourless syrup, $[\alpha]_D+39{\cdot}1°$.

Synthesis.—Fischer and Roeder (Ber. 1901, 34, 3751) synthesised uracil from acrylic acid and carbamide, these condense at 210°–220° to form dihydrourucil, which is converted by bromine into bromodihydrouracil, and this loses HBr on heating with pyridine, and yields uracil



$$\mathrm{CH}\Big\leqslant\begin{matrix}\mathrm{COOH}\\ \mathrm{CH_2}\end{matrix}+\begin{matrix}\mathrm{H_2N}\\ \mathrm{H_2N}\end{matrix}\Big>\mathrm{CO}=\mathrm{CO}\Big<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH_2}\end{matrix}\Big>\mathrm{CH_2}+\mathrm{H_2O}.$$

$$\mathrm{CO}\Big<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH_2}\end{matrix}\Big>\mathrm{CHBr}\longrightarrow\mathrm{CO}\Big<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}\Big\geqslant\mathrm{CH}.$$

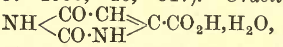
Uracil has also been prepared synthetically by Gabriel and Colman (Ber. 1903, 36, 3379) from trichloropyrimidine; and by Wheeler, Merriam, and others (Amer. Chem. J. 1903, 29, 478; J. Biol. Chem. 1905, 2, 105; Amer. Chem. J. 1907, 37, 392; 40, 547) from thiourea and ethyl sodioformylacetate. Uracil forms a colourless crystalline powder consisting of rosettes of fine needles, blackens at 280°, and melts with decomposition at 338°; it is sparingly soluble in cold, and readily soluble in hot, water, dissolves readily in ammonia, is insoluble in alcohol or ether, and is not decomposed on boiling with alkalis.

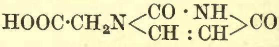
Uracil, like cytosine, gives a characteristic purple colour when dissolved in bromine water, and the solution treated with barium hydroxide solution; and, like cytosine and thymine, gives a red colour with diazobenzenesulphonic acid in the presence of alkali (*v.* Cytosine).

Salts.—Uracil forms salts in which one or two atoms of hydrogen are replaced by metals, the *sodium* salt $C_4H_3O_2N_2Na,\frac{1}{2}H_2O$ forms needles from alcohol and water; the *potassium* salt $C_4H_3O_3N_2K,H_2O$, long needles sparingly soluble in dilute alcohol; the *mercury* $C_4H_2O_2N_2Hg$ and *lead* $C_4H_2O_2N_2Pb$ salts are white precipitates, very sparingly soluble in water (Myers, J. Biol. Chem. 1910, 7, 249; Johnson and Clapp, *ibid.* 1908, 5, 49).

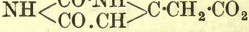
Substituted derivatives. 5-*Chlorouracil*, prepared by the action of chlorine water on uracil, has m.p. 300°–305° (Johnson, Amer. Chem. J. 1908, 40, 19); 5-*bromouracil* has m.p. 293° with decomposition (Wheeler and Merriam, *ibid.* 1903, 29, 478); 5-*iodouracil* has m.p. 272° with decomposition (Johnson and Johns, J. Biol. Chem. 1906, 1, 305); 5-*cyanouracil* forms prisms, m.p. 295° (Johnson, Amer. Chem. J. 1909, 42, 505). 5-*Nitrouracil* forms golden-yellow needles, that decompose without melting; the *potassium, ammonium, calcium, barium, zinc,* and *copper* salts are crystalline (Behrend, Annalen, 1887, 240, 1; Behrend and Grünwald, *ibid.* 1899, 309, 254; Johnson, Amer. Chem. J. 1908, 40, 19). 5-*Aminouracil* crystallises from water in thick felted needles that decompose without melting; the *nitrate* crystallises with $1H_2O$; the *picrate* has m.p. 247°–248°; the *acetyl* derivative sublimes without decomposition; the *benzoyl* derivative has m.p. 283°–287° (Behrend and Grünwald, *l.c.*; Wheeler and Bristol, Amer. Chem. J. 1905, 33, 437); 4 : 5-*diacetyldiaminouracil* sinters at 300° and decomposes at a higher temperature (Boehringer and Söhne, D. R. P. 126797). 5 : 6-*Dihydrouracil* $C_4H_6O_2N_2$ has m.p. 174°, and sublimes without decomposition at higher temperatures, crystallises in four-sided plates; the *silver* salt $C_4H_5O_2N_2Ag$ is crystalline; the *bromo* derivative $C_4H_5BrO_2N_2$ is a colourless crystalline powder, soluble in 5 parts of hot water, or 10 parts of hot alcohol (Weidel and Roithner, Monatsh. 1896, 17, 172; Tafel, Ber. 1900, 33, 3385; 1901, 34, 144; Fischer and Roeder, *ibid.* 1901, 34, 3751). 2-*Thiouracil* $C_4H_4ON_2S$, colourless prismatic plates, m.p. 340° with decomposition; 6-*thiouracil*

$$C_4H_4ON_2S,$$

small yellow needles, that blacken at 270°, melt and decompose at 328°; 2 : 6-*dithiouracil* $C_4H_4N_2S_2$, thin yellow needles, decomposing above 230° (Wheeler and Liddle, Amer. Chem. J. 1908, 40, 547). *Uracil-4-carboxylic acid*  $\mathrm{NH}\Big<\begin{matrix}\mathrm{CO\cdot CH}\\ \mathrm{CO\cdot NH}\end{matrix}\Big\geqslant\mathrm{C\cdot CO_2H,H_2O}$, has m.p. 347° (decomp.); the *ethyl ester* is obtained by the condensation of carbamide with ethyl oxalacetate; the *methyl ester* has m.p. 230° (Wheeler, *ibid.* 1907, 38, 358); *uracil-5-carboxylic acid*, colourless prisms, melts and decomposes at 278°; the *methyl ester* forms prisms that decompose at 233° (Wheeler, Johnson and Johns, *ibid.* 1907, 37, 392). *Uracil-3-acetic acid*



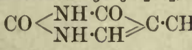
$$\mathrm{HOOC\cdot CH_2N}\Big<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CH:CH}\end{matrix}\Big>\mathrm{CO}$$

m.p. 285°, with decomposition; the *methyl ester* has m.p. 216°, the 5-*bromo* derivative melts and decomposes at 244°, the 5-*nitro* derivative melts at 264°–265° with decomposition. *Uracil-4-acetic acid*  $\mathrm{NH}\Big<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO.CH}\end{matrix}\Big>\mathrm{C\cdot CH_2\cdot CO_2H,H_2O}$ has m.p. 340°, is soluble in 8 parts of boiling, or 30 parts of cold water; the *ethyl ester* has m.p.

187°–189°; the *methyl ester* has m.p. 216°–218°; the 5-*nitro* derivative decomposes at 153° (Wheeler and Liddle, Amer. Chem. J. 1908, 30, 1152).

A large number of alkyl and aryl substituted derivatives of uracil have been prepared (Johnson and Derby, Amer. Chem. J. 1908, 40, 444; Fischer and Roeder, Ber. 1901, 34, 3759, 3762; Wheeler and Merriam, Amer. Chem. J. 1903, 29, 490; Wheeler and Bristol, *ibid.* 1905, 33, 448; Johnson and Heyl, *ibid.* 1907, 37, 628; Behrend, Annalen, 1885, 229, 8, 17; 231, 249; Behrend and Rosen, *ibid.* 1889, 251, 238; Behrend and Dietrich, *ibid.* 1889, 309, 260; Behrend and Thurn, *ibid.* 1902, 323, 166; Hagen, 1888, 244, 1; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539; Maizura, Ber. 1908, 41, 176; Johnson and Clapp, J. Biol. Chem. 1908, 5, 49; Johnson and Menge, *ibid.* 1906, 2, 105). The 5-*methyl* derivative or *thymine* is the only one that occurs among the protein degradation products.

Thymine, 5-*methyluracil*, 5-*methyl*-2 : 6-*dioxytetrahydropyrimidine*, $C_5H_6O_2N_2$,



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}>\mathrm{C\cdot CH_3}$$

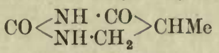
was discovered by Kossel and Neuman (Ber. 1893, 26, 2753; 1894, 27, 2215) among the products of hydrolysis of the nucleic acid from the thyroid gland; it can be similarly obtained from nucleic acids of other origin (Miescher-Schmiedelberg, Archiv. exp. Path. u. Pharm. 1896, 37, 100; Kossel, Zeitsch. physiol. Chem. 1896, 22, 188; Gulewitsch, *ibid.* 1899, 27, 292; Levene, *ibid.* 1902, 37, 402; 1903, 39, 4, 133, 479; Inouye, *ibid.* 1905, 46, 201; Mandel and Levene, *ibid.* 1905, 46, 155; 1906, 47, 140); and is also formed in the autolysis of the thyroid gland, lymph glands, and pancreas (Kutscher, Zeitsch. physiol. Chem. 1901, 34, 114; Reh, Beitr. chem. Physiol. Path. 1903, 3, 569; Levene, Zeitsch. physiol. Chem. 1905, 45, 498).

Synthesis.—Fischer and Roeder (Ber. 1901, 34, 3751) prepared 5-*methyldihydrouracil* (*hydrothymine*) by the condensation of carbamide and methyl acrylic acid, and the *bromo* derivative of this compound is converted by heating with alkali or pyridine into 5-*methyluracil* or *thymine*. Other methods of synthesis are described by Wheeler and Merriam (Amer. Chem. J. 1903, 29, 478) from ψ-methylthiocarbamide hydriodide and ethyl sodioformylpropionate; and by Gerngross (Ber. 1905, 38, 3394, 3408) from 2 : 4 : 6-trichloro-5-methylpyrimidine obtained from 5-methylbarbituric acid.

Thymine crystallises from water in four-sided plates, or stellate groups of small plates; when carefully heated it sublimes, when heated rapidly it sinters at 318°, and melts with decomposition at 321° (Fischer and Roeder, Ber. 1901, 34, 3758; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539); at 325°–335° (Johnson and Mackenzie, Amer. Chem. J. 1909, 42, 369). Thymine has a bitter taste, it is sparingly soluble in cold, readily soluble in hot water, 100 parts of water at 25° dissolve 0·404 parts, and the solution is neutral; it is sparingly soluble in alcohol or ether, and can be recrystallised from concentrated hydriodic or hydrobromic acid.

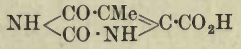
Salts.—The *potassium* $C_5H_5N_2O_2K,\frac{1}{2}H_2O$ and *sodium* salts $C_5H_5N_2O_2Na$ crystallise from dilute alcohol; the *mercury* salt $C_5H_4N_2O_2Hg$ is a white precipitate; the *lead* salt $C_5H_4N_2O_2Pb,2H_2O$ crystallises in needles (Myers, J. Biol. Chem. 1910, 7, 249).

Derivatives.—4 : 5-*Dihydrothymine*



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\ \cdot CO}\\ \mathrm{NH\cdot CH_2}\end{matrix}>\mathrm{CHMe}$$

prepared by the condensation of methyl acrylic acid with carbamide, forms microscopic crystals, m.p. 264°–265° (corr.) (Fischer and Roeder, Ber. 1901, 34, 3758). 4-*Hydroxy* 5-*nitro*-4 : 5-*dihydrothymine* $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\!-\!\!-\!\!-\\ \mathrm{NH\cdot CH(OH)}\end{matrix}>\mathrm{CMeNO_2}$, formed by rapid evaporation to dryness of a solution of thymine in fuming nitric acid, crystallises in triclinic prisms, m.p. 183°–185° (α- variety), but sometimes 230°–235° (β- variety); the sparing solubility in alcohol of this compound, as compared with the ready solubility of the nitro-derivative of uracil, forms the basis of a method of separating the two pyrimidines (Johnson, Amer. Chem. J. 1908, 40, 34; J. Biol. Chem. 1908, 4, 407). *Thymine-4-carboxylic acid*



$$\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot CMe}\\ \mathrm{CO\ \cdot NH}\end{matrix}>\mathrm{C\cdot CO_2H}$$

m.p. 328°–330°; the *potassium, lead,* and *barium* salts are crystalline; the *ethyl ester* has m.p. 255° (Johnson, J. Biol. Chem. 1907, 3, 299). *Thymine-5′-carboxylic acid* (*thymine-ω-carboxylic acid* $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}>\mathrm{C\cdot CH_2\cdot CO_2H}$, melts and decomposes at 315°–320°. The *lead* and *potassium* salts are described (Johnson and Speh, Amer. Chem. J. 1907, 38, 602).

2-*Thiothymine* $\mathrm{CS}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CH}\end{matrix}>\mathrm{CMe}$, produced by the condensation of thiourea with ethyl sodioformylpropionate, forms crystalline *sodium, potassium* and *copper* salts, and is converted quantitatively into thymine by evaporating to dryness an aqueous solution containing a slight excess of chloracetic acid (Wheeler and McFarland, Amer. Chem. J. 1910, 43, 25). 2 : 6-*Dithiothymine* $C_5H_6N_2S_2$, yellow needles, m.p. 281°, with decomposition; 6-*thiothymine*, yellow silky needles, m.p. 330° (Wheeler and McFarland, *l.c.*).

For the *alkyl* derivatives of thymine, *v.* Johnson and Clapp, J. Biol. Chem. 1908, 5, 49; Steudel, Zeitsch. physiol. Chem. 1900, 30, 539; Wheeler and McFarland, Amer. Chem. J. 1910, 43, 35; Johnson and Derby, *ibid.* 1908, 40, 456, 457.

Barbituric acid, *malonylcarbamide*, 2 : 4 : 6-*trioxyhexahydropyrimidine* $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH_2}$ was first obtained by Baeyer (Annalen, 1863, 127, 199; 1864, 130, 136) by reducing with hydrogen iodide or sodium amalgam, the compound (*dibromobarbituric acid*) prepared by the action of bromine on violuric or dilituric acid. It can be prepared by the reducing action of warm concentrated sulphuric acid on alloxantin (Finck, *ibid.* 1864, 132, 304); or synthetically by the condensation of malonic acid with carbamide in the presence of phosphoryl chloride (Grimaux, Bull. Soc. chim. 1879, [ii.] 31, 146); or of ethyl sodiomalonate with carbamide in alcoholic solution (Michael, J. pr. Chem. 1887, [ii.] 35, 456). Barbituric acid has also been prepared by the action of hot mineral or acetic or formic acid on the iminobarbituric acid obtained by the condensation of carbamide with ethyl cyanacetate in the presence of sodium ethoxide (Conrad, Annalen, 1905, 340, 310); or similarly from the *di-iminobarbituric acid* obtained from malononitrile and carbamide (Merck, D. R. P. 166448); or the *tri-iminobarbituric acid* obtained by the condensation of malononitrile with guanidine (Merck, D. R. PP. 165692, 165693); or by the condensation of ethyl malonamate with urethane (Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 171294); or by the action of alkaline condensing agents on the ureides of the half-acid esters of malonic acid

$$RO_2C\cdot CH_2\cdot CO\cdot NH\cdot CO\cdot NH_2$$

(Boehringer and Söhne, D. R. P. 193447); or by the action of ammonia on malonyl diurethane (Conrad and Schulze, Ber. 1909, 42, 729).

Barbituric acid crystallises in large colourless prisms containing $2H_2O$, becomes anhydrous in the desiccator, and decomposes on melting at 253° (Maquenne block); it is a dibasic acid forming normal and acid salts, the acidic constant $ka=10\cdot 51\times 10^{-5}$ (Wood, Chem. Soc. Trans. 1906, 1835), and the salts have the constitution represented by the formula $CO<\begin{matrix}NH\cdot C(OM)\\NH\cdot CO—\end{matrix}>CH$ (Wood and Anderson, *ibid.* 1909, 979); the *ammonium* $C_4H_3O_3N_2(NH_4)$, *potassium* $C_4H_3O_3N_2K$, *sodium* $C_4H_3O_3N_2Na$ and $C_4H_2O_3N_2Na_2,2H_2O$, *barium*

$$(C_4H_3O_3N_2)_2Ba,2H_2O,$$

copper $(C_4H_3O_3N_2)Cu,3H_2O$, and *lead*

$$C_4H_2O_3N_2Pb$$

salts are crystalline (Baeyer, Annalen, 1864, 130, 141).

1-*Methylbarbituric acid* $CO<\begin{matrix}NMe\cdot CO\\NH\cdot CO\end{matrix}>CH_2$ has m.p. 133° (Conrad, Annalen, 1905, 340, 310); 1 : 3-*dimethylbarbituric acid* crystallises in flattened needles (Mulder, Ber. 1879, 12, 465; Techow, *ibid.* 1894, 27, 3082); 1 : 3-*diethylbarbituric acid* has m.p. 52°–53° (Sembritzki, *ibid.* 1897, 30, 1814); and 1 : 3-*diphenylbarbituric acid* has m.p. 238° (Whiteley, Chem. Soc. Trans. 1907, 91, 1339).

The methylene group situated between two CO groups in barbituric acid and in its 1- and 1 : 3- substituted derivatives $CO<\begin{matrix}NR\cdot CO\\NR\cdot CO\end{matrix}>CH_2$ is highly reactive, and the hydrogen atoms can be replaced by: (1) acyl groups forming the *acyl barbituric acids* (*v. infra*); (2) halogens yielding the halogen derivatives of barbituric acid (*v. infra*); (3) hydroxyl yielding the *dialuric acids* $CO[NR\cdot CO]_2CH\cdot OH$ and the *alloxan* $CO[NR\cdot CO]_2C(OH)_2$ or $CO[NR\cdot CO]_2CO$ (*q.v.*); (4) a nitro group, yielding the *dilituric acids* $CO[NR\cdot CO]_2CH\cdot NO_2$ (*q.v.*); (5) a *nitroso group* forming the iso*nitroso barbituric acids* or violuric acids $CO[NR\cdot CO]_2C:NOH$ (*v. infra*); (6) the amino group yielding the *uramil* (*murexan*) $CO[NR\cdot CO]_2CH\cdot NH_2$ (*v. infra*), of which the sulphamino derivative is *thionuric acid*

$$CO[NR\cdot CO]_2CH\cdot NHSO_3H$$

(*v. infra*), and the carbamido derivative is *ψ-uric acid* $CO[NR\cdot CO]_2CH\cdot NH\cdot CO\cdot NH_2$ (*v. infra*); (7) alkyl groups, forming the 5- or C-*mono*-, and 5 : 5- or CC-*di-alkylbarbituric acids* $CO[NR\cdot CO]_2CHR'$ and $CO[NR\cdot CO]_2CR'R''$ (*v. infra*).

Barbituric acid and its 1- or 1 : 3-substituted derivatives also condense with aldehydes to form derivatives of the type $CO[NR\cdot CO]_2C:CHR'$ (*v. infra*), and with aromatic diazonium salts to form *hydrazones* $CO[NR\cdot CO]_2C:N\cdot NHR'$, and *azo* compounds $CO[NR\cdot CO]_2CR'N:NR''$ (*v.* ALLOXAN, and *infra*).

Acyl derivatives of barbituric acid. The acyl derivatives of barbituric acid and its 1 : 3-substituted derivatives probably have the constitution represented by the formula

$$CO<\begin{matrix}NR\cdot C(O\cdot CO\cdot R')\\NR\cdot CO———\end{matrix}>CH$$

and are to be regarded as esters of the enolic form of barbituric acid (2 : 4-*dioxy*-6-*hydroxytetrahydropyrimidine*), and not ketones of the formula $CO<\begin{matrix}NR\cdot CO\\NR\cdot CO\end{matrix}>CH\cdot COR'$ (Whiteley and Judd, private communication). The acetyl derivative of barbituric acid and of its 1 : 3-substituted derivatives occur as bye-products in the synthetic formation of the acid from malonic acid and the carbamide in the presence of phosphoryl chloride. *Acetylbarbituric acid* is a golden-yellow powder (Grimaux, Compt. rend. 1878, 87, 752; 1879, 88, 85; Conrad and Guthzeit, Ber. 1882, 15, 2844); 1 : 3-*diethylacetylbarbituric acid* $C_8H_4N_2O_3Ac$ has m.p. 62·5° (Sembritzki, *ibid.* 1897, 30, 1814); 1 : 3-*diphenylacetylbarbituric acid* $C_{16}H_{11}O_3N_2Ac$, obtained as a bye-product in the synthetic preparation of 1 : 3-diphenylbarbituric acid, also prepared by the action of acetyl chloride on the sodium salt of 1 : 3-diphenylbarbituric acid, has m.p. 150°, and forms a sparingly soluble sodium salt; 1 : 3-*diphenyl-5-ethylacetylbarbituric acid*, obtained by the action of ethyl iodide and silver oxide on the preceding compound, has m.p. 139°. 1 : 3-*Diphenylbenzoylbarbituric acid*

$$C_{16}H_{11}O_3N_2Bz,$$

prepared from benzoyl chloride and the sodium derivative of 1 : 3-diphenyl barbituric acid, has m.p. 228°; the 5-*methyl* derivative has m.p. 158°, the 5-*ethyl* derivative has m.p. 243°, and the 5-*bromo* derivative melts at 186°, and is reduced to the benzoyl compound by hydrogen iodide with the liberation of one molecular proportion of iodine (Whiteley and Judd, private communication; Whiteley, Chem. Soc. Proc. 1908, 24, 288).

Halogen derivatives of barbituric acid. *Bromo derivatives.*—The 5-mono- and 5 : 5-di-bromo derivatives of barbituric acid and its 1 : 3-substituted derivatives are reduced by hydrogen iodide, forming the original barbituric acid, and liberating iodine according to the equation

$$CO[NR\cdot CO]_2CBr_2+4HI$$
$$=CO[NR\cdot CO]_2CH_2+2HBr+2I_2,$$

the reaction is quantitative, takes place rapidly at the ordinary temperature, and affords a ready method of analysis (Whiteley, Chem. Soc. Proc. 1908, 24, 288).

5-*Bromobarbituric acid* $CO[NH\cdot CO]_2CHBr$, prepared by reducing the dibromo derivative with sodium amalgam or zinc-dust, or by heating it with aqueous prussic acid, forms small needles, sparingly soluble in water (Baeyer, Annalen, 1864, 130, 134). 5 : 5-*Dibromobarbituric acid* $CO[NH\cdot CO]_2CBr_2$, prepared by the action of bromine on barbituric, violuric, dilituric, or hydurilic acid (Baeyer, *ibid.* 1863, 127, 229), or by oxidising dibromo-oxymethyluracil with fuming nitric acid (Behrend, *ibid.* 1886, 236, 62), forms sparingly soluble rhombic crystals, m.p. 234° (decomp.). 5-*Bromo-5-methylbarbituric acid* has m.p. 192·5° (corr.), Fischer and Dilthey, *ibid.* 1904, 335, 334.

1 : 3-*Diethyl*-5 : 5-*dibromobarbituric acid*

$$CO[NEt\cdot CO]_2CBr_2$$

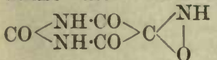
has m.p. 86°–87° (corr.) (Sembritzki, Ber. 1897, 30, 1814). 1 : 3-*Diphenyl*-5 : 5-*dibromobarbituric acid* $CO[NPh\cdot CO]CBr_2,C_6H_6$, m.p. 152°; the benzene-free compound has m.p. 160° (Whiteley, Chem. Soc. Trans. 1907, 91, 1347); 5-*bromo*-1 : 3-*diphenylbenzoylbarbituric acid* has m.p. 186° (Whiteley, Chem. Soc. Proc. 1908, 24, 288).

Chloro derivatives.—5 : 5-*Dichlorobarbituric acid*, by the oxidation of dichloro-oxymethyluracil, crystallises in prisms or plates, $a : b : c = 0·7766 : 1 : 0·8929$ (Behrend, *ibid.* 1886, 236, 57). 5 : 5-*Dichloro*-1 : 3-*dimethylbarbituric acid*, obtained by treating amalic acid (tetramethylalloxantin) with phosphoric chloride, has m.p. 157° (Techow, Ber. 1894, 27, 3082). 5 : 5-*Dichloro*-1 : 3-*diethylbarbituric acid* has m.p. 87·5° (corr.) (Sembritzki, *ibid.* 1897, 30, 1814).

***iso*Nitroso derivatives of barbituric acids. Violuric acids.** Violuric acid or *iso*nitrosobarbituric acid is so called because, although colourless in the solid state, and forming colourless alkyl ethers, it shows a violet colour in solution in pure water, and gives rise to intensely coloured (red, violet, blue, green, and yellow) salts with metals and substituted ammonias (Wagner, Zeitsch. physikal. Chem. 12, 314; Guinchard, Ber. 1899, 32, 1723; Donnan and Schneider, Chem. Soc. Trans. 1909, 95, 956; Zerewitinoff, Ber. 1909, 42, 4802). Hantzsch and his pupils have shown that polychromatism and chromotropism are exhibited by some of the violurates, and they are of opinion that the violuric acids and their colourless ethers are the true oximino ketones $CO<^{NR\cdot CO}_{NR\cdot CO}>C : NOH$, whilst the *blue* violurates are the nitroso-enolic salts $CO<^{NR\cdot CO}_{NR\cdot C(OM)}\geqslant C\cdot NO$, and the more positive the nature of the metallic radicle present and the solvent, the more completely are the violuric acids as true oximino-ketones transformed into the structurally isomeric nitroso-enols (Ber. 1899, 32, 575; Guinchard, *ibid.* 1723; 1909, 42, 966; 986, 1000; 1910, 43, 45; 82). Another explanation of the differences in constitution between the colourless violuric acids and the coloured violurates is to regard the latter as derivatives of the oxime

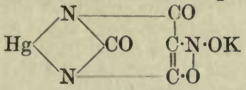
$$CO<^{NH\cdot CO}_{NH\cdot CO}>C : NOH,$$

whilst the colourless acids are *iso*-oximes



(Lowry, Brit. Assoc. Reports, 1904, 222; Hartley, Chem. Soc. Trans. 1905, 87, 1816; Baly, *ibid.* 1906, 89, 981; Whiteley, *ibid.* 1907, 91, 1331).

Violuric acid $CO[NH\cdot CO]_2C : NOH,H_2O$, prepared by the action of nitrous acid or nitric acid (sp.gr. 1·2) on hydurilic acid (Baeyer, Annalen, 1863, 127, 200); by treating barbituric acid with potassium nitrite (Baeyer, *ibid.* 1864, 130, 140); by heating dilituric acid with glycerol, or by warming its iron salt with potassium cyanide; or by the action of hydroxylamine hydrochloride on alloxan (Ceresole, Ber. 1883, 16, 1133; Pellizzari, Gazz. chim. ital. 1887, 17, 258), is a monobasic acid, and decomposes acetates; it also yields a pale flesh-coloured *mercuric* derivative, the potassium salt



of which is deep violet, becoming blue when anhydrous (Auld, Chem. Soc. Trans. 1907, 91, 1047). The *methyl ether* $C_4H_2O_3N_3\cdot CH_3$ is colourless, and has m.p. 270° (Guinchard, Ber, 1899, 32, 1723); the *benzyl ether* $C_4H_2O_3N_3\cdot C_7H_7$ is also colourless, and has m.p. 222° (Hantzsch and Isherwood, *ibid.* 1909, 42, 986).

1-*Methylvioluric acid* $C_5H_5O_4N_3,H_2O$ decomposes carbonates and acetates (Andreasch, Monatsh. 1900, 21, 281). 1 : 3-*Dimethylvioluric acid* $CO[NMe\cdot CO]_2C : N\cdot OH,H_2O$ has m.p. 124°, the anhydrous substance melts at 141° (Techow, Ber. 1894, 27, 3084; Andreasch, Monatsh. 16, 17; Whiteley, Chem. Soc. Trans. 1903, 83, 19); the benzyl ether $C_{13}H_{13}O_4N_3$ has m.p. 164° (Hantzsch and Isherwood, *l.c.*). 1 : 3-*Diethylvioluric acid* $CO[NEt\cdot CO]_2C : NOH,H_2O$ melts at 90° and loses H_2O at 107° (Sembritzki, Ber. 1897, 30, 1814). 1 : 3-*Diphenylvioluric acid* $CO[NPh\cdot CO]_2C : N\cdot OH$ has m.p. 227°; the *acetyl* derivative $C_{16}H_{10}O_4N_3Ac$ melts and decomposes at 245° (Whiteley, Chem. Soc. Trans. 1907, 91, 1339).

Amino derivatives of barbituric acids. *Uramil* (*murexan*), 5-*amino*-2 : 4 : 6-*trioxyhexahydropyrimidine* $CO<^{NH\cdot CO}_{NH\cdot CO}>CH\cdot NH_2$, was originally prepared by boiling alloxantin with ammonium chloride or ammonium thionurate with hydrochloric acid (Liebig and Wöhler, Annalen, 1838, 26, 310); it is formed together with alloxan and ammonia when murexide is decomposed by acids (Beilstein, Annalen, 1858, 107, 183), or by caustic alkalis (Reoch, Chem. News, 1875, 32, 171); and is obtained when alloxanphenylhydrazone is reduced with tin and hydrochloric acid (Kühling, Ber. 1898, 31, 1973). Uramil is conveniently prepared by reducing nitro- or nitrosobarbituric acid with hydriodic acid (Baeyer, Annalen, 1863, 127, 223); or by heating ammonium dialurate, closed vessels being employed to avoid oxidation (Piloty and Finckh, *ibid.* 1900, 333, 71). Uramil forms silky needles, insoluble in cold, sparingly soluble in hot, water, it gives murexide on long boiling with ammonia; it has heat of combustion +380 Cal., and heat of formation +170·7 Cal. (Matignon, Ann. Chim. Phys. [vi.] 28, 289). Uramil forms metallic derivatives in which the iminohydrogen atoms are replaced by metals, *potassium uramil* $CO[NK\cdot CO]_2CH\cdot NH_2,2H_2O$, obtained in slender pale-yellow needles by dissolving uramil in warm 50 p.c. potassium hydroxide solution, is converted by iodine into potassium murexide, and by methyl iodide into 1 : 3-dimethyluramil; the *acid potassium salt* $C_4H_5O_3N_3,C_4H_4O_3N_3K$ forms colourless sparingly soluble leaflets; the *barium* and *lead* salts have also been prepared. 7-*Acetyluramil* forms crystalline salts, of which the *potassium*, *ammonium*, *silver*, *barium*, *lead*, and *copper* salts are described. 7-*Methyluramil* $CO[NH\cdot CO]CH\cdot NHMe$ is prepared from alloxantin and methylamine acetate; the *ethyl* derivative

$C_4H_4N_3O_3Et$ is similarly prepared (Piloty and Finckh, Annalen, 1900, 333, 71; *cf.* Fischer, Ber. 1897, 30, 561). 5-*Methyluramil*

$$CO[NH{\cdot}CO]_2CMe{\cdot}NH_2,$$

m.p. 237° (corr.) is prepared by treating 5-bromo-5-methylbarbituric acid with alcoholic ammonia; 5-*ethyluramil* has m.p. 216° (corr.) (Fischer and Dilthey, Annalen, 1904, 335, 334). 1-*Methyl-uramil* is prepared from methylalloxan and ammonium sulphite (Fischer, Ber. 1897, 30, 3091). 1 : 3-*Dimethyluramil*

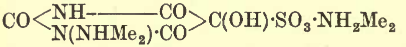
$$CO[NMe{\cdot}CO]_2CH{\cdot}NH_2,$$

decomposes at 200° (Techow, *ibid.* 1894, 27, 3087). 1 : 3 : 7-*Trimethyluramil* decomposes at 200° (Fischer, *ibid.* 1897, 30, 559). 1 : 3-*Diethyluramil* decomposes at 200° (Sembritzki, *ibid.* 1897, 30, 1814). 1 : 3-*Diphenyluramil*, m.p. 97°, forms a crystalline hydriodide readily soluble in cold water, with dissociation into hydrogen iodide and the uramil (Whiteley, Chem. Soc. Trans. 1907, 91, 1340).

Thionuric acid. *Sulphaminobarbituric acid* $CO[NH{\cdot}CO]_2CH{\cdot}NH{\cdot}SO_3H,1\frac{1}{2}H_2O$ is prepared by heating alloxan or violuric acid with a solution of ammonium sulphite (Liebig and Wöhler, Annalen, 1838, 26, 268; Baeyer, *ibid.* 1863, 127, 210). The free acid obtained by decomposing the lead salt with sulphuretted hydrogen is a crystalline mass, readily soluble in water, forming a strongly acid solution; it is a dibasic acid yielding acid and normal salts, and is hydrolysed on boiling with water, yielding uramil and sulphuric acid. 1 : 3-*Dimethylthionuric acid* is obtained as its ammonium salt

$$CO[NMe{\cdot}CO]_2CH{\cdot}NH{\cdot}SO_3NH_4,2H_2O$$

by heating at 100° a solution of 1 : 3-dimethylalloxan with ammonium sulphite and ammonium bicarbonate (Techow, Ber. 1894, 27, 3086), the salt loses $2H_2O$ at 105°, and decomposes at 180°; the *barium salt* $C_6H_7N_3O_6SBa$ is also described. The *dimethylamine salt*



$$CO<\begin{matrix}NH{-}{-}{-}{-}{-}CO\\N(NHMe_2){\cdot}CO\end{matrix}>C(OH){\cdot}SO_3{\cdot}NH_2Me_2$$

is obtained when alloxan is treated in aqueous solution with a neutral solution of dimethylamine sulphite, it is decomposed by dilute acids yielding sulphur dioxide, alloxantin, and dimethylamine, but no trace of substituted uramil (Piloty and Finckh, Annalen, 1904, 333, 71).

ψ-Uric acid, *carbamidobarbituric acid*

$$CO[NH{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

prepared by boiling aminobarbituric acid with potassium cyanate (Baeyer, *ibid.* 1863, 127, 3), or heating it with carbamide at 180° (Grimaux, Bull. Soc. chim. 1879, [ii.] 31, 535), forms prisms, sparingly soluble in cold water, and is converted by fusing with anhydrous oxalic acid, or by boiling with 25 p.c. hydrochloric acid, into uric acid. Pseudouric acid is a monobasic acid, and the *ammonium* $C_5H_5N_4O_4NH_4,H_2O$; *potassium* $C_5H_5N_4O_4K,H_2O$; *sodium*

$$C_5H_5N_4O_4Na,2H_2O;$$

barium $(C_5H_5N_4O_4)_2Ba,5H_2O$; *calcium; lead* $(C_5H_5N_4O_4)_2Pb,2H_2O$; *copper* and *mercury* salts are crystalline. 7-*Methylpseudouric acid* $CO[NH{\cdot}CO]_2CH{\cdot}NMe{\cdot}CO{\cdot}NH_2$ is prepared from 7-methyluramil and potassium cyanate (Fischer, Ber. 1897, 30, 562). 1 : 3-*Dimethylpseudouric acid* $CO[NMe{\cdot}CO]_2CH{\cdot}NH{\cdot}CO{\cdot}NH_2$ has m.p. 210° (Techow, *ibid.* 1894, 27, 3088). 1 : 3 : 7-*Trimethylpseudouric acid* decomposes between 180° and 190°, when slowly, and at 195° when rapidly heated (Fischer, *l.c.*). 1 : 3-*Diethylpseudouric acid* has m.p. 196° (corr.) with decomposition (Sembritzki, *ibid.* 1897, 30, 1823). 1 : 3-*Diphenylpseudouric acid* melts and decomposes at 217° (Whiteley, Chem. Soc. Trans. 1907, 91, 1341).

5-Mono- and 5 : 5-Di-alkyl derivatives of barbituric acid. The following general methods have been employed for the preparation of the 5-mono- and 5 : 5-di-alkyl barbituric acids, or as they are sometimes called the C-alkyl or CC-dialkyl-barbituric acids: (1) Direct alkylation of the barbituric acid by the action of the alkyl halide on the silver salt (Conrad and Guthzeit, Ber. 1881, 14, 1643; 1882, 15, 2844; Gebrüder von Niessen, D. R. P. 144432). (2) Condensation of the *ethyl ester* of the *alkyl malonic acid* with (*a*) *carbamide* in the presence of sodium ethoxide, the alkali metal or its amide (Merck, D. R. PP. 146948, 147278, 147279, 147280; Fischer and Dilthey, Annalen, 1904, 335, 334); (*b*) *biuret* or *alkyl allophanate* (Merck, D. R. P. 183857); (*c*) *carbamide* in the presence of alkali or alkaline earth carbides (Merck, D. R. P. 185963); (*d*) *guanidine* and subsequent hydrolysis of the 2-iminobarbituric acid obtained (Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 189076). (3) Condensation of *alkyl malonyl chloride* with (*a*) *carbamide* (Merck, D. R. P. 146949); (*b*) *guanidine* and subsequent hydrolysis with dilute acid of the 2-iminobarbituric acid obtained (Merck, D. R. P. 158890); (*c*) *urethane* and the conversion of the diurethanes into the barbituric acid by heating with alkyl oxides, hydroxides or fuming mineral acids (Traube, D. R. PP. 171992, 172885, 172886); (*d*) with *alkyl allophanates* (Merck, D. R. P. 177694). (4) Condensation of the *alkyl malonitrile* with: (*a*) *guanidine* and subsequent hydrolysis of the 2 : 4 : 6-tri-iminobarbituric acid thus obtained (Merck, D. R. PP. 165692, 165693); (*b*) *carbamide, thiocarbamide or guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, D. R. P. 185963). (5) Condensation of *dialkylmalonamides* with (*a*) *alkyl carbonates* in the presence of alkali ethoxides (Farbenfabriken vorm. Friedr. Bayer & Co., D. R. PP. 163136, 168406, 168407); (*b*) *oxalyl chloride* (Einhorn, D. R. P. 225457). (6) By the action of acid condensing agents on the tetrasubstituted diureides of the dialkylmalonic acids $CX_2(CO{\cdot}NH{\cdot}CO{\cdot}NR_2)_2$ (Einhorn, D. R. P. 193446). (7) By the action of alkali condensing agents on the ureides of the half acid esters of alkylmalonic acids

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CRR'{\cdot}CO_2R''$$

(Boehringer and Söhne, D. R. P. 193447). (8) Condensation of *ethyl dialkylcyanacetate* with: (*a*) *carbamide* in the presence of sodium ethoxide, and subsequent hydrolysis of the 4-iminobarbituric acid thus obtained (Merck, D. R. PP. 156384, 156385); (*b*) *carbamide* or *thiocarbamide* and subsequent hydrolysis of the imino or thioiminobarbituric acid thus obtained by heating with mineral, formic, or acetic acids (Conrad, Annalen, 1905, 340, 310); (*c*) *guanidine* in the presence of various condensing agents, and subsequent hydrolysis of the 2 : 4-di-iminobarbituric acid thus obtained (Farbenfabriken vorm Friedr. Bayer & Co., D. R. P. 158592;

Chemische Fabrik auf Aktien, vorm. E. Schering, D. R. P. 201244; Basler Chemische Fabrik, D. R. P. 204795); (*d*) *dicyanodiamides* in the presence of alkali condensing agents and subsequent hydrolysis of the substituted barbituric acid thus obtained (Farbenfabriken vorm, Friedr. Bayer & Co., D. R. P. 165223); (*e*) *carbamide, thiocarbamide*, or *guanidine* in the presence of the carbides of the alkali or alkali earth metals (Merck, D. R. P. 185963).

The following 5-substituted alkyl derivatives of barbituric acid are described: the 5-*methyl*, m.p. 202°–203° (Fischer and Dilthey, Annalen, 1904, 335, 334); the 5-*ethyl*, m.p. 194° (Merck, D. R. P. 165693); the 5-*propyl*, m.p. 207°–208°; the 5-iso*propyl*, m.p. 216°; the 5-*benzyl*, m.p. 206° (Conrad and Guthzeit, Ber. 1882, 15, 2844); the 5:5-*dimethyl*, m.p. 279°; the 5-*methyl*-5-*ethyl*, m.p. 212°; the 5-*methyl*-5-*propyl*, m.p. 182°; the 5:5-*diethyl* or *veronal*, m.p. 191° (corr.) (*q.v.* and SYNTHETIC DRUGS); the 1-*methyl*-5:5-*diethyl*, m.p. 154·5°; the 1-*phenyl*-5:5-*diethyl*, m.p. 197°; the 1:3:5:5-*tetraethyl*, b.p. 125·5°–126°/8·8 mm.; the 5-*ethyl*-5-*propyl*, m.p. 146; the 5:5-*dipropyl* or proponal, m.p. 146° (Fischer and Dilthey, *l.c.*; Merck, D. R. P. 156385), 166° (Conrad, Annalen, 1905, 340, 310) (*v.* SYNTHETIC DRUGS); the 5:5-*di*-iso*butyl*, m.p. 173·5°; the 5:5-*di*-iso*amyl*, m.p. 172°; the 5:5-*dibenzyl*, m.p. 222° (Fischer and Dilthey, *l.c.*).

Condensation of barbituric acids with aldehydes and ketones. Barbituric acid and its 1- and 1:3-substituted derivatives condense readily, in the absence of condensing agents, with aldehydes or with dichloroketones to form alkylidene derivatives of the types

$$CO[NH{\cdot}CO]_2C:CHR \text{ and}$$

$CO[NH{\cdot}CO]_2C:CRR'$, which on reduction yield the corresponding 5-alkylbarbituric acids

$$CO[NH{\cdot}CO]_2CH{\cdot}CH_2R \text{ and}$$

$CO[NH{\cdot}CO]_2CH{\cdot}CHRR'$. 5-*Benzylidenebarbituric acid* $CO[NH{\cdot}CO]_2C:CHPh$, m.p. 256°; and o-*nitrobenzylidenebarbituric acid*, m.p. 250°–252°, are colourless; *cinnamylidenebarbituric acid*, m.p. 226°–228°, and *furfurylidenebarbituric acid*, m.p. above 280°, are yellow (Conrad and Reinbach, Ber. 1901, 34, 1339); p-*hydroxybenzylidenebarbituric acid*, m.p. 300°, is canary-yellow, and p-*dimethylaminobenzylidenebarbituric acid*, m.p. 282°, is orange-red (Weinschenk, *ibid.* 1685).

1:3-*Diphenyl*-5-*benzylidenebarbituric acid* $CO[NPh{\cdot}CO]_2C:CHPh$ exists in two forms, the stable form being yellow, and the labile form being colourless, each melts at 214°; 1:3-*diphenyl*-5-*cinnamylidenebarbituric acid*

$$CO[NPh{\cdot}CO]_2C:CH{\cdot}CH:CHPh,$$

m.p. 268°, is orange-yellow; 1:3-*diphenyl*-5-*diphenylmethylenebarbituric acid*

$$CO[NPh{\cdot}CO]_2C:CPh_2,$$

m.p. 264° is deep yellow. Each of the compounds described above contains the complex $\begin{smallmatrix}\cdot CO\\ \cdot CO\end{smallmatrix}{>}C:CRR'$, consisting of three chromophores, yet each is coloured or colourless according to the nature of the radicles R and R′. It would seem that when R is hydrogen and R′ phenyl or its ortho- substituted derivative the compound is usually colourless, but that it is yellow when R′ is a para- substituted derivative of phenyl, or a more highly unsaturated radicle such as that afforded by cinnamaldehyde or furfuraldehyde; when both R and R′ are phenyl groups the compound is also yellow (Whiteley, Chem. Soc. Trans. 1907, 91, 1332).

Condensation of barbituric acids with aromatic diazonium chlorides. Barbituric acid and its 1:3-substituted derivatives condense readily with aromatic diazonium salts to form the aryl hydrazone of the corresponding alloxan, the same compound being obtained by the condensation of the arylhydrazine with the corresponding alloxan, or the 5:5-dibromoderivative of the barbituric acid

$$\left.\begin{array}{l}CO[NH{\cdot}CO]_2CH_2 + ClN:NPh \searrow\\ CO[NH{\cdot}CO]_2CO + H_2N{\cdot}NHPh \rightarrow\\ CO[NH{\cdot}CO]_2CBr_2 + H_2N{\cdot}NHPh \nearrow\end{array}\right. CO[NH{\cdot}CO]_2C:N{\cdot}NHPh$$

(*v.* ALLOXAN)

When 5-substituted derivatives of barbituric acid condense with aromatic diazonium salts the products are azo compounds of the type $CO[NR{\cdot}CO]_2CR'N:NR''$, these are readily hydrolysed by mineral acids yielding nitrogen, and the phenol corresponding with the aromatic diazonium salt, and regenerating the barbituric acid

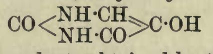
$$CO[NR{\cdot}CO]_2CR'N:NR'' \rightarrow CO[NR{\cdot}CO]_2CHR' + N_2 + R''OH.$$

5-*Benzeneazo*-1:3-*diphenyl*-5-*benzylbarbituric acid* $CO[NPhH{\cdot}CO]_2C(CH_2Ph){\cdot}N:NPh$, m.p. 170°–171°, forms bright yellow prisms; the p-*nitro* derivative crystallises in bright yellow prisms, m.p. 181°–182°; 5-*benzeneazo*-1:3-*diphenyl*-5-*diphenylmethylbarbituric acid*

$$CO[NPh{\cdot}CO]_2C(CHPh_2){\cdot}N:NPh,$$

bright yellow prisms, m.p. 160°; the p-*nitro* derivative forms canary-yellow prisms, m.p. 175° (Whiteley, Chem. Soc. Trans. 1907, 91, 1344).

*iso***Barbituric acid**, 5-*hydroxyuracil*



$$CO{<}\begin{matrix}NH{\cdot}CH\\ NH{\cdot}CO\end{matrix}{>}C{\cdot}OH$$

is one of the products obtained by the reduction of nitrouracil; it forms an *acetyl* derivative, and when treated with bromine water yields *iso*dialuric acid (*q.v.*) (Behrend and Roosen, Ber. 1888, 21, 999). M. A. W.

PYRITES, COPPER, *v.* COPPER-PYRITES.

PYRITES (*Ger.* Kies). The ancient name πυρίτης, from πῦρ, fire, was no doubt applied to a variety of minerals, which possess, in common with flint, the property of striking fire. In more recent times the name 'pryites' has been used for a variety of sulphide minerals possessing a metallic lustre and a fair degree of hardness; and the wide range it covered is well indicated by the title of J. F. Henckel's book 'Pyritologia, oder Kiess-Historie (Leipzig, 1725); English translation Pyritologia; or, a History of the Pyrites, the principal body in the Mineral Kingdom. In which are considered its names, species beds, and origin; its iron, copper, unmetallic earth, sulphur, arsenic, silver, gold, original particles, vitriol, and use in smelting (London, 1757).' At the present day the word enters into many compound names, both popular and scientific, of minerals, *e.g.* iron-pyrites or sideropyrite, copper-pyrites or chalcopyrite, arsenical pyrites or arsenopyrite (=mispickel), magnetic pyrites (=pyrrhotite), tin-pyrites (=stannite), cobalt-pyrites (=linnæite), capillary pyrites (=millerite), white pyrites (=mispickel and marcasite), cockscomb- and spear-pyrites (=marcasite), nicopyrite (=pentlandite), argentopyrite, leucopyrite, &c.; whilst in modern German 'kies' is used still more freely in compound names.

Iron-pyrites (Ger. *Eisenkies*, *Schwefelkies*), in English often called simply 'pyrites,' and by American and French writers 'pyrite.' Iron disulphide (FeS_2) is dimorphous, crystallising either in the cubic or in the orthorhombic system; the former modification is the mineral iron-pyrites and the latter is marcasite (*q.v.*).

Crystals of iron-pyrites are of common occurrence, and they are often beautifully and sharply developed. Their degree of symmetry is that of the pentagonal-dodecahedral (or parallel-faced hemihedral) class of the cubic system. Common forms are the cube, octahedron, and pentagonal-dodecahedron, or combinations of these. The pentagonal-dodecahedron with the indices (210) is, indeed, so characteristic of this mineral that it is known as the pyritohedron. The faces of the cube are each striated parallel to only one of their edges, and in such a manner that on three adjacent faces the three sets of striations are perpendicular to one another; this, again, is an extremely characteristic feature of crystals of iron-pyrites. Disseminated grains and compact masses are abundant; the mineral also occurs in nodular and stalactitic forms often with an internal radio-fibrous structure. The thermo-electrical properties of iron-pyrites are of interest; some crystals are more strongly thermo-electrically positive than antimony, and others more negative than bismuth, so that the two when placed together give a stronger thermo-electric couple than do antimony and bismuth.

The mineral is opaque with a brass-yellow colour and a bright metallic lustre; its streak is greenish- or brownish-black. There is no distinct cleavage; the mineral is brittle, and breaks with a conchoidal to uneven fracture. The hardness is 6–6½; the mineral scratches glass, and is itself scratched by a knife only with difficulty. These characters enable iron-pyrites to be readily distinguished from other yellow metallic minerals with which it is sometimes confused, *e.g.* copper-pyrites (H. =3½–4, with a deeper yellow colour), and gold (H.=2½–3 and malleable). From marcasite the distinction is less easy in the absence of any distinct crystalline form, for the hardness and colour are nearly the same; marcasite is, however, sometimes rather paler in colour and its sp.gr. (4·8) is a little lower than that of iron-pyrites (4·9–5·1).

When pure, iron-pyrites contains sulphur 53·4, and iron 46·6 p.c. Small quantities of other metals are, however, often present, *e.g.* copper, silver, gold, nickel, cobalt, zinc, tin, thallium, tellurium, selenium, arsenic, &c. But it is probable that these are due to the mechanical admixture of other minerals; for example, in the abundant cupriferous ores of Spain and Norway 1–5 p.c. of copper is present as admixed copper-pyrites. In many gold-mining districts auriferous iron-pyrites is of considerable importance as an ore of gold. The Spanish ores, after roasting for sulphur and extraction of copper from the residues, yield about 1 oz. of gold per 300 tons of ore. The following are analyses of pyritic ore from the more important districts where it is mined: I. Rio Tinto, Huelva, Spain; II. San Domingos, Algarve, Portugal; III. Sain-Bel, dep. Rhône, France; IV. Meggen, Westphalia; V. Röros, Trondhjem, Norway; VI. Chestatee, Dahlonega district, Georgia (E. C. Eckel, Bull. U.S. Geol. Survey, 1903, No. 213, 63).

	I.	II.	III.	IV.	V.[1]	VI.[2]
S .	48·50	48·90	46·40	45·60	49·00	43·52
Fe .	40·92	43·55	39·00	38·52	42·35	39·70
Cu .	4·21	3·10	1·50	—	2·48	3·09
Zn .	0·22	0·35	—	6·00	2·01	0·72
Pb .	1·52	0·93	—	0·64	0·24	—
As .	0·33	0·47	0·10	trace	nil	nil
SiO_2 .	3·46	0·73	9·25	8·70	1·85	9·26
Al_2O_3 .	—	—	3·75	—	1·25	2·53
CaO .	0·90	0·20	—	—	0·23	—
H_2O .	—	0·70	—	—	—	0·36
	100·06	98·93	100·00	99·46	99·63	99·61

During the grinding of pyrites for analysis it is found that the material suffers a certain amount of oxidation (*see* E. T. Allen and J. Johnston, The Exact Determination of Sulphur in Pyrite and Marcasite, J. Ind. Eng. Chem. 1910, 2, 196).

Iron-pyrites burns in the air with a small bluish flame, and is capable of supporting its own combustion; the products are sulphur dioxide and ferric oxide (the 'purple ore' or 'blue billy' of iron smelters). This is of importance in the roasting of iron-pyrites for the manufacture of sulphuric acid, and in the 'pyritic smelting' of cupriferous ores. When heated out of contact with the air, the mineral begins to decompose at about 500°, and finally one-half of the sulphur is expelled.

Many experiments have been made on iron-pyrites and marcasite with the object of detecting a difference in their chemical constitution, but the results are not concordant. H. N. Stokes (Amer. J. Sci. 1901, 12, 414; Bull. U.S. Geol. Survey, 1901, No. 186, 1–50) has devised a chemical method for discriminating between these minerals and for their quantitative determination in mixtures. This method depends on the fact that when iron-pyrites or marcasite is boiled with an excess of a solution of a ferric salt to complete reduction of the latter, the ratio of the sulphur oxidised to mineral decomposed is perfectly definite and characteristic of each mineral, provided certain standard and easily controllable conditions are observed. With a boiling solution of ammonium-iron alum containing 1 gr. of ferric iron and 16 c.c. of 25 p.c. free sulphuric acid per litre, the percentage of sulphur oxidised in iron-pyrites is about 60·4, and in marcasite about 18 of the total sulphur. These figures are the characteristic oxidation coefficients, which depend, however, on the temperature and concentration of the solution. The determinations are made in an atmosphere of carbon dioxide, with specially designed apparatus. It is shown, for example, that the nodules, often supposed to be marcasite, so abundant in the chalk-marl at Folkestone, Kent, are really iron-pyrites; one specimen was found to contain iron-pyrites 97 and marcasite 3 p.c.

Iron-pyrites is a mineral of extremely wide distribution. It is found in rocks of all kinds and of all geological ages, either scattered as isolated grains, nodules, and crystals, or collected in veins and large lenticular masses. The best crystallised specimens are from the magnetite mines at Traversella in Piedmont, and the hæmatite mines of Rio in the island of Elba. Good crystals have also been found in the mineral-veins of Cornwall and many other mining districts. The deposits of cupriferous iron-pyrites, which are so extensively mined, occur as large lenticular masses in slaty rocks near their contact with igneous rocks. Such deposits are mined at Rio Tinto, Tharsis, Calañas, &c., in the Spanish province of Huelva, and San Domingos in the neighbouring Portuguese province of Algarve; at Sain-Bel, dep. Rhône, France; Rammelsberg in the Harz, and Meggen in Westphalia; Sulitjelma in Arctic Norway and Röros in southern Norway; Brosso in Piedmont, Italy; Pilley's Island, Newfoundland; Louisa Co. and Prince William Co. in Virginia, and elsewhere in the United States. The world's production amounts to about five million tons per annum; of which Spain contributes two-thirds and Portugal, France, Germany, Norway, and the United States each about a quarter of a million tons per annum.

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[1] Also MgO, 0·22.

[2] Also MgO, 0·43.

When subjected to weathering processes near the earth's surface, iron-pyrites is readily decomposed, producing cellular masses of limonite—the so-called gozzans and iron cappings of lodes—which are valuable indications of the presence of metalliferous deposits. At the same time, any gold present in the pyrites is set free, giving a 'free-milling' ore. Two types of the alteration of iron-pyrites may be distinguished. By oxidation in the presence of pure water it gives ferrous sulphate (melanterite), free sulphur, and sulphuric acid; and the latter by its action on the surrounding rocks produces gypsum, various alums, &c. When the oxygenated water contains calcium carbonate in solution the sulphur is removed in the soluble form of gypsum, leaving the iron behind in the form of hydroxide; in this way have been formed the abundant pseudomorphs of limonite and goethite after iron-pyrites.

The principal use of iron-pyrites is for the production of sulphur dioxide in the manufacture of sulphuric acid and in the sulphite wood-pulp process of the paper-maker. It is also used in the preparation of sulphur by simple distillation. The residues after roasting are treated for the extraction of copper, silver, and gold, and finally of iron; to a limited extent they are also used in the making of red paints. By exposing iron-pyrites in heaps to the weather ferrous sulphate (copperas) is prepared in considerable quantities. Pyritous shales, the so-called alum-shales, are utilised in the manufacture of alum. Trivial uses of the mineral are in cheap jewellery, particularly in France and Ireland. It is hard, and takes a fine polish. Polished plates of iron-pyrites, probably used as mirrors, have been found in the graves of the ancient Incas of Peru. In olden times it was used in tinder-boxes and in the wheel-locks of guns.

L. J. S.

PYROACETIC ACID *v.* ACETIC ACID.

PYROCATECHIN, PYROCATECHOL, *v.* PHENOL AND ITS HOMOLOGUES.

PYROCATECHOL-*o*-CARBOXYLIC ACID *v.* PROTOCATECHUIC ACID.

PYROCHLORE *v.* COLUMBIUM.

PYROCOLL *v.* BONE OIL.

PYROCRESOLS $C_{15}H_{14}O$. A group of isomeric bodies, three in number, discovered by Schwarz in coal-tar, and more particularly examined by Bott (J. Soc. Chem. Ind. 1887, 646).

α-Pyrocresol crystallises in large shining plates, exhibiting a bluish-green fluorescence; readily soluble in benzene, chloroform, carbon tetrachloride, carbon disulphide, &c.; less so in acetic acid, alcohol, or ether; and insoluble in water and alkalis. Soluble also without action in acetyl chloride, phosphorus trichloride, or solution of phosgene gas. M.p. 196°; readily sublimes.

β-Pyrocresol. Melts at 124°, and crystallises in small needles or laminæ.

γ-Pyrocresol differs from its isomers by its extreme solubility in all solvents; it invariably crystallises in needles, m.p. 104°–105°, and does not sublime.

These three pyrocresols have also been obtained from the last fraction of the distillate from crude carbolic acid (Zmerzlikar, Monatsh. 1910, 31, 897).

On oxidation with chromic acid in acetic acid solution the pyrocresols yield compounds having the empirical formula $C_{15}H_{12}O_2$.

α-Pyrocresol oxide, m.p. 168°, forms yellowish needles; very soluble in acetic acid and alcohol. According to Zmerzlikar (*l.c.*), this oxide, when fused with potash, yields *m*-cresol, *m*-hydroxytoluic acid and *m*-hydroxyterephthalic acid. It is therefore identical with 4 : 4′-dimethylxanthone and α-pyrocresol is 4 : 4′ dimethyl, xanthane.

β-Pyrocresol oxide, m.p. 95°.

γ-Pyrocresol oxide, m.p. 77°, crystallises in small rhombic plates, which turn red on exposure to light.

On gentle reduction with hydrogen iodide, the oxides yield pyrocresols, and on very energetic reduction they are decomposed, forming the same reduction products as the pyrocresols themselves, namely, chiefly an oil of formula $C_{15}H_{32}$.

α-Tetranitro-pyrocresol oxide $C_{15}H_8(NO_2)_4O_2$, crystallises from nitrobenzene or glacial acetic acid in small yellowish plates, which, on heating, burn with a flash. Is insoluble in caustic potash, and sparingly soluble in alcohol.

β-Tetranitro-pyrocresol oxide resembles the α- compound, but is more soluble in alcohol.

γ-Tetranitro-pyrocresol oxide forms a granular mass of a pale yellow colour. More soluble in alcohol than the α- compound.

Halogen and sulpho derivatives have also been prepared. α-*Dibromopyrocresol* $C_{15}H_{12}Br_2O$ is obtained in the form of thick, elongated plates; m.p. 215°.

PYRODINE, *Acetylphenylhydrazine, hydracetin,* $C_6H_5{\cdot}N_2H_2{\cdot}C_2H_3O$, was first synthesised by Liebermann. A white crystalline powder, m.p. 128°–130°, very sparingly soluble in cold water and in ether, readily so in hot water, and in alcohol. It possesses very little taste.

Pyrodine is prepared by the interaction of phenylhydrazine with acetic anhydride (Fischer, Annalen, 1877, 190, 129), or with thioacetic acid

(Pawlewski, Ber. 1897, 31, 662), and also by other methods (Just, *ibid.* 1886, 19, 1202; Bamberger, *ibid.* 1897, 31, 2630; Leighton, Amer. Chem. J. 20, 677; Baidakowski and Slepak, J. Russ. Phys. Chem. Soc. 35, 71). It is a powerful antipyretic. It reduces fever temperature quickly, and maintains the temperature at a low level for some hours, producing marked perspiration, but not nausea, vomiting, or collapse. It is especially applicable in cases of pneumonia, scarlet fever, and typhus. Given in small doses in the latter disease it enables the patient to pass through the fever at a low temperature range without delaying the crisis, and it seems also to shorten the period of convalescence. It is less applicable in cases of typhoid, owing to the early exhibition of toxic symptoms. Given in often repeated doses at short intervals it easily shows toxic properties, and these depend on the action on the blood, producing hæmoglobinæmia. It should not be given (unless the temperature be very high) oftener than once in 18 or 24 hours, and it is not safe to continue its use for more than a few days. The dose for children is 2–4 grains, for adults 8–12 grains. It is a much more powerful antipyretic than either antipyrine, antifebrine, or phenacetin; but it is also much more toxic than these bodies. This disadvantage is reduced by the fact that it is rarely necessary to give more than one dose in 12 to 18 hours, as the temperature is kept low for a longer period than by any of the other antipyretics. It reduces the pulse as well as the temperature, and often causes diuresis (J. Dreschfeld, J. Soc. Chem. Ind. 1888, 765; Merck, *ibid.* 1889, 476).

The isomeric acetyl compound,

$$C_6H_5N(COCH_3)NH_2$$

has m.p. 125°–126° (Pechmann and Runge, Ber. 1894, 27, 1695; Widman, *ibid.* 2964; Busch and Frey, *ibid.* 1903, 36, 1364).

PYROGALLOL (pyrogallic acid, 1:2:3-trihydroxybenzene) $C_6H_3(OH)_3$ is obtained by the dry distillation of gallic acid (Braconnot, Annalen, 1832, 1, 26; Pelouze, *ibid.* 1834, 10, 159); by fusing hæmatoxylin (Meyer, Ber. 1879, 12, 1392), or α- or β-*p*-chlorophenol sulphonic acid with caustic potash (Peterson and Baehr-Predari, Annalen, 1871, 157, 136, 150). In the form of its methyl ethers it also occurs in beechwood tar creosote (Hofmann, Ber. 1878, 11, 333; Rosauer, Monatsh. 1898, 19, 557).

Preparation.—Gallic acid is heated in a bronze digester with 2 or 3 times its weight of water, at 200°–210°, for about half an hour, in such a manner that the carbon dioxide can readily escape. The resulting pyrogallol solution is heated with animal charcoal, filtered, and rapidly evaporated. The pyrogallol which crystallises out may then be further purified by sublimation or distillation under reduced pressure (Luynes and Esperandieu, Compt. rend. 1865, 61, 487; *see* also D. R. PP. 30648, 32830; Seurbach, Ber. 1877, 10, 38). Gallic acid (10 grms.) may also be heated with glycerol (30 grms.), at 190°–200°, until carbon dioxide ceases to be evolved (Thorpe, Chem. News. 1881, 43, 109). The yield in both these cases is almost theoretical. Pyragallol may also be prepared by heating gallic acid with 2 parts of coarsely powdered brimstone (Liebig, Annalen, 1857, 101, 48), or with twice its weight of aniline at 120°; the *aniline pyrogallate*, m.p. 55°–56°, so obtained is treated with benzene or toluene, when pure pyrogallol is precipitated (Cazeneuve, Compt. rend. 1892, 114, 1485), or by heating pyrogallol-4-sulphonic acid with dilute mineral acids in a sealed tube for 8 hours at 200° (D. R. P. 207374; Frdl. 1907–10, 143).

Properties.—Pyrogallol forms white lustrous laminæ or fine needles, m.p. 132·5°–133·5°, b.p. 292°–294° at 730 mm. (decomp.). It is odourless, has a bitter taste, and is poisonous. It is readily soluble in alcohol, ether, and in water, dissolving in 2½ parts of water at 13°. When exposed to air its aqueous solution turns brown rapidly, but its alcoholic solution turns brown more rapidly when kept in a stoppered bottle; both solutions may, however, be preserved indefinitely by the addition of a small quantity of sodium bisulphite (Lumière and Seyewetz, J. Soc. Chem. Ind. 1908, 183). The alkaline solution also turns brown on exposure to air owing to the absorption of oxygen, and this property is made use of in the estimation of oxygen; unless, however, a sufficient excess of alkali is present, much carbon monoxide is evolved (Clowes, Chem. Soc. Proc. 1895, 200; *see* also Liebig, Annalen, 1851, 77, 107; Weyland and Zeitler, *ibid.* 1880, 205, 264; Weyl and Goth, Ber. 1881, 14, 2666; Calvert, Compt. rend. 1863, 57, 873 Cloëz, *ibid.* 875; Boussingault, *ibid.* 886; Berthelot, *ibid.* 1898, 126, 1459; also art. ANALYSIS).

Under the influence of the silent electric discharge small quantities of hydrogen and carbon monoxide are evolved.

When hydrogenated in the presence of finely divided nickel, cyclo-hexane-1:2:3-triol, m.p. 67°, is formed (Sabatier and Mailhe, Compt. rend. 1908, 146, 1196).

When dissolved in baryta water and shaken with air, it forms hexahydroxydiphenyl (Harries, Ber. 1902, 35, 2954), whilst when oxidised electrolytically it yields purpurogallin (Perkin, Chem. Soc. Trans. 1904, 244). The latter is also obtained together with a substance $C_{12}H_{10}O_7$ when an alcoholic solution of pyrogallol is treated with acetic acid, then with *iso*amyl nitrite, and the product boiled with water (Perkin and Steven, *ibid.* 1906, 802).

Pyrogallol rapidly reduces gold, silver, and mercury salts even in the cold. Pure ferrous salts, when added to aqueous pyrogallol, gives a white turbidity, which becomes blue on addition of sodium hydroxide or in the presence of a trace of ferric salt. In the absence of alkali the blue colour rapidly changes to red-brown, this change also being induced by the addition of mineral acids. Organic iron salts also give a blue colouration (Hirsch, Chem. Zentr. 1899, i. 927). When agitated with potassium cyanide pyrogallol gives a yellow-red colouration, which turns to yellow-brown on addition of hydrogen peroxide (Griggi, Chem. Zentr. 1899, i. 454). In this way it can be distinguished from gallic acid, which gives a ruby-red colour with the first reagent, and from digallic acid, which gives a dirty white with the second.

Five mgrms. of pyrogallol dropped on to a melted mixture of 45 of ammonium nitrate, 34 of lead nitrate, and 21 of lead oxide produces a chrome-green colour (Mathieu-Plessy, Bull. Soc. Ind. Mulhouse, 1890, 69).

When treated with strong sulphuric acid and alcoholic tartaric acid, pyrogallol yields a liquid which first exhibits violet striæ, and then assumes a uniform intense violet colour. On dilution with water the violet colour disappears. If lactic acid is used instead of tartaric, an orange-red colour is obtained, which does not disappear on dilution (Carletti, Boll. Chim. Farm. 1909, 48, 441).

With formalin and sulphuric acid, pyrogallol gives a red colour (Endemann, J. Soc. Chem. Ind. 1896, 791); in the presence of ammonia water a product, used in the treatment of bad smelling wounds, ulcers, &c., is formed (D. R. P. 99570; Frdl. 1907–1910, 724). When heated with aldehyde and sulphuric acid, it forms a crystalline compound $C_8H_8O_3,2H_2O$ (Causse, Bull. Soc. Chim. [iii] 3, 861).

When pyrogallol is heated with benzaldehyde in the presence of zinc chloride or of fuming sulphuric acid, red substances, having the properties of aurine dyes, are formed (Hofmann, Ber. 1893, 26, 1139).

An aqueous solution of pyrogallol is turned brown by nitrous acid, and is oxidised by nitric acid to carbon dioxide and oxalic acid (Rösing, J. 1857, 315; Jacquemin, Bull. Soc. Chim. 1873, 21, 435; *see* also Oppenheimer, Ber. 1903, 36, 1744).

Derivatives.—Pyrogallol monosulphonic acid $C_6H_2(OH)_3HSO_3$ is obtained by treating pyrogallol with sulphuric acid of sp.gr. 1·84 at about 100° (Delage, Compt. rend. 1900, 131, 450; Schiff, Annalen, 1875, 178, 171; *see* also D. R. P. 207374; Frdl. 1907–10, 143); by treating the product with fuming sulphuric acid, the *disulphonic acid* is obtained (Delage, *ibid.* 1901, 132, 421). The mono- acid acts as a dibasic acid, whilst the disulphonic acid acts as a tribasic acid, this being due to the fact that one of the hydroxyl groups in pyrogallol is acidic (Delage, *ibid.* 1901, 133, 297).

When solutions of the hydroxide of calcium, barium, or strontium are added to the corresponding pyrogallol mono-, or di-sulphonate, coloured substances are produced, the composition of which varies with the conditions of the experiment. Six such compounds have been obtained, varying in colour from violet to blue. They are soluble in acids, giving yellow solutions, and their solubility in water and in alcohol increases with increasing molecular weight of the base and the number of sulphonic groups. They oxidise rapidly in the moist state, but when dry are fairly stable. When deposited on silk they turn green, then yellow (Delage, Compt. rend. 1903, 136, 893, 1202; also *ibid.* 760 and *l.c.*).

Pyrogallol sulphonic acid has been employed in dyeing hair (D. R. P. 185041; Frdl. 1907–10 851). The sulphonic acids also combine with nitroso aromatic and aryl amines, forming gallocyanine sulphonic acids, which give blue to violet shades on wool (D. R. PP. 203145, 214063; Frdl. 1907–10, 247, 253).

For amino and nitro derivatives, *see* Schiffer, Ber. 1892, 25, 721.

Pyrogallol carboxylic acid. *See* Gallic acid.

Pyrogallol carbothioxylic acid

$C_6H_2(OH)_3CS_2H,H_2O$

forms beautiful glistening golden scales which become anhydrous at 70° and have m.p. 154° (Lippmann, Monatsh. 1889, 10, 617).

Pyrogallol monomethyl ether $C_6H_3(OH)_2OMe$ is obtained by fusing guaiacol sulphonic acid with sodium hydroxide. It has m.p. 66°–67°, and dissolves in aqueous alkali with a green colour, which gradually turns brown. It reduces silver nitrate, especially on warming (D. R. P. 109789).

Pyrogallol dimethyl ether $C_6H_3(OMe)_2OH$ can be isolated from beechwood tar creosote by treating the fraction boiling at 250°–270° with benzoyl chloride and decomposing the product with alkali (Hofmann, Ber. 1878, 11, 1455; *ibid.* 1879, 12, 1377, 2216; Rosauer, Monatsh. 1898, 19, 557; D. R. P. 9328).

Pyrogallol dimethyl ether is obtained pure by heating syringic acid at 240°–270°. It forms crystals, m.p. 54·8°, b.p. 262·7° (*see* also D. R. P. 162658, and Rosauer, *l.c.*). It yields a *picrate*, m.p. 61°, and an *acetyl* derivative, m.p. 53·5°, and when oxidised with sodium nitrite in acid solution, or by other oxidising agents, it is converted into *cedriret* (Graebe and Hess, Annalen, 1905, 340, 232). When mixed with the dimethyl ether of methyl pyrogallol and caustic soda and oxidised by heating in air at 200°, it yields pittacall or eupittonic acid, which dyes silk orange in an acid bath, but is of little value as a dye (Hofmann, *l.c.*). Colouring matters are also obtained when the pyrogallol ethers are treated with chloroform, carbon tetrachloride, or hexachlorethane in the presence of alkalis. When the dimethyl ether is treated with tiglic aldehyde, a resin, $C_{21}H_{26}O_6$, is obtained (Doebner Arch. Pharm. 1896, 234, 610).

Freshly prepared pyrogallol dimethyl ether can be employed as a delicate reagent for the detection of chromic acid, ferric salts, nitrous acid, and other oxidising agents, with which it gives a red or yellow colouration (Meyerfeld, Chem. Zeit. 1910, 34, 948).

The *trimethyl ether* (Will, Ber. 1888, 21, 607; Perkin, Chem. Soc. Trans. 1896, 1241; Boyd and Pitman, *ibid.* 1905, 1255) and the *ethyl ethers* (Hofmann, Ber. 1878, 11, 798; Hirschel, Monatsh. 1902, 23, 181; D. R. P. 162658). For other alkyl ethers, *see* Herzig and Pollack (Monatsh. 1902, 23, 700; *ibid.* 1904, 21, 505 and 808; Ber. 1903, 36, 660).

The *carbamic esters* of pyrogallol-1 : 3-dialkyl ethers are prepared by treating the ethers with carbamic chloride ($ClCONH_2$) in ethereal solution or by the interaction of phosgene with a salt of pyrogallol dialkyl ether and then converting the chloroformic acid ester of the pyrogallol ether so formed into the carbamic acid ester by the action of ammonia (D. R. P. 194034; Frdl. 1907–10, 917).

Pyrogallol and its alkyl ethers combine with chloracetic acid on boiling with sodium hydroxide in a reflux apparatus. The condensation product separates on acidifying with hydrochloric acid, and may be recrystallised from water (D. R. P. 155568; Frdl. 1902–1904, 102.

Pyrogallol glycollic acid m.p. 153°–154°, *pyrogallol diglycollic acid*, *pyrogallol ethyl ether diglycollic acid*, m.p. 108°–109°, and *pyrogallol diethyl ether glycollic acid*, m.p. 82°–83°, have been prepared. Unlike pyrogallol, these derivatives are not poisonous, and can be used in the treatment of skin diseases. They are also said to be useful in photography and in the manufacture of dyestuffs.

Pyrogallol (20 parts) reacts with succinic anhydride (10 parts) at 150°–170°, using zinc chloride as condensing agent; it yields amongst other dyestuffs, pyrogallol succineïn, an analogue of galeïn and digallacyl, which gives yellow colours with alumina and grey with iron mordants (Georgievics, Monatsh. 1899, 20, 450).

Pyrogallol succineïn $C_{16}H_{14}O_8$, purified by means of its sulphuric acid compound, forms a red powder, almost insoluble in ordinary solvents, and decomposes at 180°. It combines with 1 molecule of hydrochloric acid to form brownish plates.

Digallacyl, $C_{16}H_{14}O_8$, crystallises from alcohol in needles or plates, and turns dark at 270° without melting. It dissolves in soda lye, forming a yellow solution, which on oxidation turns greenish and deposits a yellow flocculent precipitate. Digallacyl dissolves in strong sulphuric acid with a yellow colour, and on heating or adding ferric chloride the solution turns an intense violet colour. On careful dilution, a greenish precipitate is formed, which on filtration and treatment with sulphuric acid again gives a violet solution.

Pyrogallol benzeïn, $C_{38}H_{24}O_{11}$, is obtained by heating benzotrichloride with pyrogallol. The chloride so formed is decomposed by boiling it with water, and the benzeïn is recrystallised from glacial acetic acid. Its dyeing properties are of little importance. A number of its derivatives have been prepared (Doebner and Foerster, Annalen, 1890, 257, 60). *Hydropyrogallol benzeïn* $C_{19}H_{14}O_5,3H_2O$, formed by the reduction of the above compound, forms reddish needles. A dyestuff is also obtained by the action of acet-*p*-toluidine on pyrogallol in the presence of phosphorus oxychloride (D. R. P. 140421; Frdl. 1902–1904, 349), and violet to blue dyestuffs are formed by the interaction of pyrogallol with a number of *p*-dialkylamino-*o*-hydroxybenzobenzoic acids in the presence of sulphuric acid (D. R. P. 122359; Frdl. 1900–1902, 280).

Pyrogallol forms condensation products with acetone and with methyl ethyl ketone (Fabinezi and Szeki, Ber. 1905, 38, 3527).

Pyrogallol forms additive products with aliphalic amines, and some of these are used in photography. *Dimethylamine pyrogallol* $C_6H_3(OH)_3{\cdot}NHMe_2$ crystallises in prisms, m.p. 163°, dissolves readily in water, is sparingly soluble in alcohol, and insoluble in ether. *Trimethylamine pyrogallol* melts at 160° (D. R. P. 141101; Frdl. 1900–1902, 1218).

Pyrogallol also combines with gallocyanine (D. R. P. 77452; Frdl. 1894–1897, 496), with a number of diazo compounds (D. R. PP. 81109, 81376, 8266; Frdl. 1890–1894, 637, 648; *ibid.* 1894–1897, 797, 798), and with other compounds forming useful dyes (D. R. PP. 4914, 50450; 50451, 54661, 72446, 58483, 59863, 61326; Frdl. 1890–1894, 120, 147, 150, 272; 1887–1890, 481–485).

Monoacetyl pyrogallol (*Eugallol*)

$$C_6H_3(OH)_2O{\cdot}COCH_3$$

is obtained by heating the tri- or the di- acetate with pyrogallol to about 160°. It distils at 185°/25 mm. (D. R. PP. 104663, 122145; Frdl. 1900–1902, 1119).

Diacetyl pyrogallol has m.p. 110°–111° (D. R. P. 104663).

Triacetyl pyrogallol (*lenigallol*), obtained by heating pyrogallol (200 parts) with acetic anhydride (500 parts) and 1 part of strong sulphuric acid, is a white crystalline powder, m.p. 165° (D. R. P. 124408; Frdl. 1900–1902, 1119; Perkin and Simonsen, Chem. Soc. Trans. 1905, 858). The acetyl compounds are employed in medicine.

Pyrogallol (2 mols.) reacts with vanillin (1 mol.), forming *pyrogallol vanilleïn* $C_{20}H_{18}O_8$, colourless crystals which turn intensely blue with a minute trace of hydrochloric acid (Etti, Monatsh. 1882, 8, 677).

Caffeine-pyragallol

$$C_8H_{10}O_2N_4,C_6H_6O_3,4H_2O$$

is formed by mixing equivalent quantities of the constituents in warm aqueous solutions. It consists of needle-shaped crystals, m.p. 70° (Ultée, Chem. Zentr. 1910, i. 519).

Pyrogallol aldoxime forms white lustrous plates, m.p. 203°–204° (D. R. P. 114195; Frdl. 1900–1902, 121).

Alloxan pyrogallol needles or prisms, which decompose at 230° (D. R. PP. 107720, 113722; Frdl. 1900–1902, 163).

Pyrogallol carbonate $HO{\cdot}C_6H_3{<}\substack{O\\O}{>}CO$, colourless needles, m.p. 132°–133°, is formed by passing phosgene gas into a solution of pyrogallol in a mixture of pyridine and xylene. If more phosgene is employed, *dipyrogallol tricarbonate* $CO(O.C_6H_3{<}\substack{O\\O}{>}CO)_2$, colourless leaflets, m.p. 177°, is formed (Einhorn, Cobliner, and Pfeifer, Ber. 1904, 37, 100). The benzoyl, methyl, bromo, nitro, and other derivatives of the carbonate are described by these authors. Fuming nitric and sulphuric acids convert the carbonate into 4 : 6-*dinitropyrogallol*

$$C_6H(NO_2)_2(OH)_3$$

m.p. 208°. It also combines with quinoline triethylamine, and other substances.

Pyrogallol piperidine $C_5H_{11}N,C_6H_6O_3$, forms white needles which evolve gas at 110°, become discoloured at 140°, and melt at 171° (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 142).

Pyrogallol-antipyrine $C_6H_3(OH)_3,C_{11}H_{12}N_2O$ separates as an oil on mixing concentrated solutions of pyrogallol and antipyrine. It forms colourless crystals, m.p. 77°–78° (Patein and Dufau, Bull. Soc. chim. 1897, [iii.] 15, 1048).

Pyrogallol quinoline. See PURPUROGALLIN.

Pyrogallol glycoisoquinoline forms small rose-coloured hexagonal plates and yields a *hydrochloride* and a *platinochloride.*

Pyrogallolglycotetrahydroquinoline

$$C_6H_2(OH)_3CO{\cdot}CH_2{\cdot}C_9NH_{10}$$

forms yellow crystals, m.p. 177°–178°. It yields amorphous yellow metallic salts, does not combine with acids, and gives a crystalline *sulphonic acid* derivative, m.p. 188°. With phenylhydrazine, it forms the compound $C_6H_2(OH)_3C(N{\cdot}NHPh)CH_2{\cdot}NH{\cdot}NHPh$, which crystallises in slender, yellow, silky needles, m.p. 214°–215° (Nencki, Ber. 1894, 27, 1969).

Pyrogallol also combines with naphthoquinone, yielding products which are employed in pharmaceutical and dyestuff preparations (D. R. P. 96565; Frdl. 1897–1900, 671).

For *halogen* derivatives of pyrogallol, *see* Will (*l.c.*), Peratonner (Gazz. chim. ital. 28, i. 227), Biétrix (Compt. rend. 1896, 122, 1545), Perkin and Simonsen (*l.c.*).

For the metallic derivatives, *see* Causse and Bayard (Compt. rend. 1892, 115, 507), De Forcrand (*ibid.* 46), Causse (*ibid.* 1893, 117, 232), Godeffroy (Chem. Zentr. 1895, ii. 159), Kunz and Krause (Arch. Pharm. 1898, 236, 542). A number of other derivatives of pyrogallol have been described (Dzierzgowski, Ber. 1894, 27, 1988; Bistrzycki and Oehlert, *ibid.* 2632; Syniewski, *ibid.* 1895, 28, 1874; Dimroth and Zoeppritz, *ibid.* 1902, 35, 993; Godeffroy, J. Soc. Chem. Ind. 1895, 650; Bartolotti, Gazz. chim. ital. 1896, 26, ii. 433; *ibid.* 1897, 27, i. 289; Rosauer, *l.c.*; Graebe and Suter, Annalen, 1905, 340, 222; Gattermann, *ibid.* 1907, 357, 313; Perkin and Weizmann, Chem. Soc. Trans. 1906, 1649). *V.* also PHENOL AND ITS HOMOLOGUES.

For the use of pyrogallol in photography, *v.* art. PHOTOGRAPHY.

PYROGUAIACIN *v. Guaiacum*, art. RESINS.

PYROLIGNATES, PYROLIGNEOUS ACID, *v.* ACETIC ACID.

PYROLUSITE. An important ore of manganese, consisting essentially of manganese dioxide (MnO_2); but being amorphous and a final product of the decomposition of other manganese minerals, it is frequently more or less impure. It forms earthy to granular masses with an iron-black to steel-grey colour and submetallic lustre; the streak is bluish-black, and the mineral is soft enough (H.=2) to soil the fingers. Sometimes it shows a fibrous or columnar structure, or crystals more or less distinct in form. These are, however, pseudomorphous forms, and are due to the alteration of crystallised manganite to pyrolusite. Manganese dioxide crystallises in the tetragonal system, and is represented by the rare mineral polianite. Pyrolusite occurs, together with psilomelane (*q.v.*) and other black manganese oxides, usually as beds and pockets in clay overlying limestones, or as a weathering product of crystalline rocks rich in manganese silicates. The known localities are numerous. The ore is mined at the Lindener Mark near Giessen, Ilmenau in Thuringia, Vorderehrensdorf in Moravia, Platten in Bohemia, Carnarvonshire and Merionethshire in North Wales; and more extensively in the Caucasus and elsewhere in Southern Russia, Greece, Brazil, United States, India, &c. (On the manganese ore deposits of India, *see* L. L. Fermor, Mem. Geol. Survey, India, 1909, 37.)

The name pyrolusite (from πῦρ, fire, and λύειν, to wash) has reference to the well-known use of the mineral in decolorising glass. Other applications in which the mineral acts as an oxidising agent are in the preparation of chlorine, bromine, and oxygen; in electric batteries; as a dryer in varnishes and paints; and in the manufacture of manganates and permanganates used as disinfectants. As a colouring material, it is used in the manufacture of green and violet paints; in the colouring of glass, pottery and pottery glazes, and bricks; and in dyeing and calico-printing. The principal use, however, of the mineral at the present day is in the manufacture of iron and steel; the ore being used either directly in the smelting or at some later stage in the form of ferromanganese or spiegeleisen. It is also used for the manufacture of manganese-bronze and some other alloys.

L. J. S.

PYROMETRY. The first attempt to record temperatures for industrial purposes may be said to have been made by Josiah Wedgwood in 1782. The instrument he devised depended on the permanent contraction of fire-clay when subjected to a high temperature, and remained the standard for nearly a century. In 1882 the famous Sèvres pottery employed fusible clay to determine the temperature necessary for their work. This method was perfected in 1886 by Seger, who constructed cones of clay of varying composition with fusing points ranging from 600° to 1800°. The substances which enter into the composition of these cones are essentially pure quartz sand, Norwegian felspar, carbonate of lime, Zettlitz kaolin, consisting of silica, alumina, oxide of iron and water. In very fusible cones oxide of iron, oxide of lead, carbonate of soda and boric acid are added. The less fusible cones contain calcined alumina. These cones are extensively used to-day, chiefly on account of their simplicity and cheapness. The cones are in the form of triangular pyramids about 15 mm. on a side and 50 mm. high. Under the action of heat they finally soften and bend. The desired temperature is reached when the apex has bent halfway over and points downwards. A further increase of temperature causes the cone to melt completely. The fusing-points of the various mixtures have been carefully determined at the Berlin porcelain works by comparison with an accurate pyrometer. The cones are supplied by number, the less fusible for high temperatures extend from 1 to 38, the highest being about 1980°. The more fusible are numbered from 01 to 022, the lowest temperature being at 590°. The cones 28 to 38 are derived from cone 27 by the addition of increasing quantities of Al_2O_3. The cones 5 to 28 from the cone 5 by the addition of increasing quantities of the mixture $Al_2O_3+10SiO_2$. Cones 1 to 5 from cone 1 by replacing increasing quantities of sesquioxide of iron by alumina. For the other series of cones Nos. 010 to 1 are obtained from cone 1 by the substitution of boric acid for silica. Cones 022 to 011 are derived from cone 022 by the addition of increasing quantities of the mixture

$$Al_2O_3+2SiO_2.$$

While these cones are useful for the attainment of any particular temperature in a furnace, they can be no guide in maintaining a steady temperature, and can be successfully used only in such cases where a furnace is carried to the desired point and then allowed to cool off. In the ceramic industry they are generally used, and before firing a series of cones is introduced so that the attainment of successive temperatures may be observed by the falling over of the tips of the various cones in order of fusibility. As general temperature indicators, they are undoubtedly useful, and even in cases where more expensive means are adopted to measure the temperature of a furnace. Other forms of fusion pyrometers have been devised from time to time. Coils of wire of the various metals have been used, such as the Prinsep alloys (range 620°–1225°) (Ann. Chim. Phys. 1829, 41, 247); but these are less easily observed, and give by no means so fine a method of indicating temperatures as the Seger cones.

Brearley and Moorwood's sentinel pyrometers (Jour. Iron and Steel Inst. 1907, 68, 261) have been prepared for steel-hardening furnaces. These depend on the precise character of the melting-point of pure sodium or potassium chlorides. These salts are cast into cylinders and placed in small porcelain saucers upon the floor of the furnace or oven to be controlled. When the temperature rises, the potassium chloride cylinder remains erect, and retains its form absolutely until 735°–736° is exceeded and 740° is reached, when it melts down to a clear liquid. In the same way sodium chloride and barium chloride melt in their turn. In order to cover the range from 630° to 770°, various combinations of sodium chloride and potassium chloride have been made. The gradual addition of potassium chloride, or *vice versâ,* lowers the melting-point until with 1 molecule of each salt the lowest attainable point is reached. Other ranges of temperature may be observed among different salts. Thus mixtures of sodium and potassium sulphates give a range from about 800°–1050°. The indications of the sentinels are sharper than the Seger cones, which gradually soften at first and often leave some doubt as to the exact temperature attained.

The observation of the boiling-point of liquid alloys of sodium and potassium has been suggested by Baly and Chorley. This may be used up to 600°, but cannot be said to be a form of measurement suitable for industrial purposes.

General Expansion Methods.

The measurement of temperature by the expansion of various materials forms the basis of a large number of instruments. With the exception of the ordinary air or hydrogen thermometer, all the commercial instruments are empirical in character. It is hardly within the scope of this article to deal with the standard gas thermometer. It should be understood, however, that all the temperature indications of the commercial instruments should be expressed in terms of the normal hydrogen scale. While local conditions may be adequately met by individual scales easily reproduced, these are but makeshifts, and should be replaced by standard instruments or by reference to a standard pyrometer.

The well-known mercury-in-glass thermometer is adapted for ranges higher than the boiling-point of mercury by the use of hard glass or quartz and the introduction of nitrogen under pressure into the tube. Commercial instruments are available reading to 500°C. or 600°C., but the pressure is so high (30 atmospheres or more) that they are exceedingly liable to break.

The use of bars of metal has been in vogue for a very long time, and many different forms of instruments have been devised. One often met with at the present time is that of Schäffer and Budenberg. It consists of an outer tube of iron surrounding a rod of copper attached at the end. The tubes are usually 2 ft. 6 ins. long, attached to a dial gauge for showing the relative expansion of the two metals. The relative movement of the metals is magnified by a system of levers. The range of the instrument is from 212°F. to 720°F. Some other forms such as those of Daniell, Steinle and Harting employ bars of metal inclosed in earthenware and graphite respectively, and may be used for much higher temperatures.

Various practical air pyrometers have been proposed. The pyrometer of Heisch and Folkard is a simplified air thermometer reading only to 500°C. The form of air pyrometer devised by Wiborgh (Trans. A. I. Min. E. 1892; also Jour. Iron and Steel Inst. 1882, 2, 110) consists of a porcelain bulb containing air at suitable initial pressure. The bulb is attached to a metal tube communicating with a collapsible vessel operating a registering device similar to a Bourdon steam gauge. The increase in air pressure due to rise of temperature is effective in operating the gauge, on which a scale of temperature is placed, ranging from ordinary temperature up to 2400°F. The instrument is similar in appearance to the metal expansion thermometer, and, like it, is subject to errors due to the magnifying device for producing a large open scale. It is, however, more fragile owing to the porcelain bulb, and the scale has to be set frequently when the pyrometer is cool.

The Bristol air pyrometer is well-known in America, and has the advantage of combining a recording gauge. The bulb is metallic, and is attached to many feet of flexible metallic tubing. It is not used, however, for temperatures over 500°F. or 600°F.

The expansive power of the vapour of many liquids above their normal boiling-points has been highly recommended as a suitable means for measuring high temperatures. Thus Schäffer and Budenberg's thalpotassimeter is a type of instrument employing this method. It is similar in appearance to their metal expansion thermometer, but the increase in pressure of the vapour is used as in Wiborgh's air thermometer to operate a pressure gauge. For temperatures of 92°F. to 250°F., ether is employed as the source of vapour, from 212°F. to 650°F. water is used, and from 650°F. to 1400°F. mercury is the working substance. Whilst it may be said that the first two are serviceable, it cannot be said that the last one is durable enough for practical purposes, on account of the destructive action of the mercury vapour on the metal parts.

Transpiration pyrometers. A pyrometer has been devised by Frews which in principle is a continuous air thermometer. The pressure of air flowing out of a fine opening in a tube is adjusted when cold. When the tube is heated the back pressure, which results from the volume increase, is recorded, and gives a measure of the temperature.

The best known transpiration pyrometer is that of Uehling and Steinbart (Stahl u. Eisen, 1899, 19, 431: Jour. Iron and Steel Inst. 1904, 65, 124) (*see* Fig. 1). Air, carefully filtered, is drawn through a fine opening in the end of a fine platinum tube surrounded by a second platinum tube exposed to the heat of the furnace. This air is sucked through a second fine tube after being cooled down to a temperature of 212°F. A steam-blast exhaust serves to maintain a constant suction. It is obvious that owing to the suction of the air a difference in pressure will result between the two sides of the second fine tube. Owing to the expansion of the air passing through the first heated tube, this difference in pressure decreases with rising temperature, and a suitable manometer tube may be used as an indicator of the temperature of the heated air. The rising and falling column of water in the manometer tube indicates on a scale a rising and falling temperature. The pyrometer can readily be made self-recording by attaching a float over the liquid in the manometer tube. To the float is attached gear which operates a pen moving over a rotating drum. The instrument has extensive use in blast-furnace work, in spite of its high cost. This is chiefly due to the permanent character of the installation. The pyrometer is not portable, and hence there is less liability of breakage in transferring it from one furnace to another.

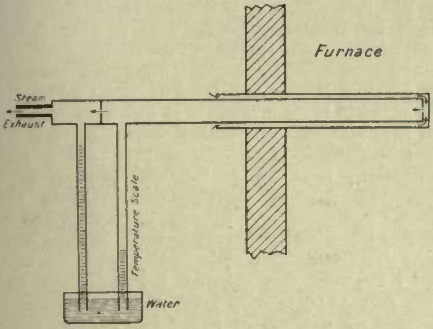


Fig. 1.

A transpiration pyrometer, known as the Krupp's pyrometer (von Bergen, Jour. Iron and Steel Inst. 1886, 1, 207, also known as the Hobson hot-blast pyrometer), has been devised by which ordinary mercury thermometers can be used to measure the temperature of the hot blast. Cool air in suitable proportions is mixed with a stream of the hot gases drawn out through a side tube in the hot-blast main. It is based on the assumption that the ratio of the amount of hot gas to cold air is the same, whatever the pressure of the hot blast.

Specific heat pyrometer. While at one time most of the best pyrometric methods were based on the measurement of the heat absorbed by a known mass of metal immersed in a furnace, at the present time there appears to be little reason for their continuation.

The water pyrometer of Siemens is based on this principle, and was formerly widely used for industrial purposes. It seems hardly necessary to more than mention it here, since it has been practically superseded by more modern and more convenient methods.

The conducting of heat out of a furnace by a metal rod such as Jourde's method has been used to indicate the temperature of the furnace. This method cannot, however, be said to be of industrial application.

Wiborgh's thermophone pyrometer consists of small calcined cylinders which are placed in the furnace and explode with a sharp crack at the end of an interval of time corresponding to the temperature of the furnace. Their range is from 600°F. to 4000°F. In practice they are placed in the furnace, and the time up to the moment of explosion gives a means of calculating from a table the temperature.

Electrical pyrometry. Electrical pyrometers may be divided into two classes, those making use of the thermoelectric properties of the metals first discovered by Seebeck in 1820 and applied by Becquerel in 1830, and those in which the change in resistance of a metal wire with temperature is employed. It is to the researches of C. Barus (Bull. U.S. Geol. Survey, 1889, 54; Phil. Mag. 1892, [v.] 34, 1) and Le Chatelier (Bull. Soc. Chem. 1887, 47, 2, 300) that we owe our knowledge of the most serviceable high-temperature thermoelectric pyrometer. Barus experimented with wires of platinum and an alloy of platinum and 10 p.c. iridium. He found that the junction of the pure metal and the alloy formed a thermocouple of great reliability over the range 300°–1500°C. Le Chatelier studied a junction of platinum with an alloy of platinum and 10 p.c. rhodium. Subsequent researches by A. L. Day and by Holborn and Day (Wied. Ann. 1899, 68, 817; Drude's Ann. 1901, 4, 99) have shown that the rhodium alloy stands the high temperature better. From the thermoelectric table of the metals pairs of metals may be selected giving large electromotive forces, but exhaustive research has found none to equal the couple of Le Chatelier in standing the destructive action of even a moderately high temperature for any length of time.

They are all based on the same general principle. One end, the hot junction, is composed of the two metals fused or soldered together, and the other end consists of the cold junction, where the wires, having passed out of the furnace, are maintained at a uniform temperature either at a 0°C. or at the temperature of the room. From the 'cold end,' wires pass to a galvanometer or millivoltmeter, and the temperature may be indicated directly on the scale. The modern development of the portable galvanometer has very much facilitated the use of the thermojunction. The correctness of reading depends as much on the cold end as on the hot end, and hence great care must be exercised to have the wires of the couple sufficiently long to be away from the influence of the furnace. This is an expensive matter with the platinum thermocouple, but the use of a water-cooled 'cold end' helps to correct this disadvantage. The E.M.F. developed in microvolts for the platinum-rhodium and platinum-iridium thermocouple is given in the following table:—

Temp.	Ir.	Rh.
100°C.	517	565
448°C.	3228	3450
930°C.	11000	8500
1500°C.		15100

The expression found to hold for the Reichsanstalt standard junction which is usually supplied is given in microvolts as follows, to hold only between 300°F. and 1100°F.

$$E = -310 + 8{\cdot}048t + 0{\cdot}00172t^2$$

when the cold junction is maintained in melting ice.

In obtaining temperatures by one of these couples it is much more practical to determine accurately a number of fixed points, measuring at the same time the E.M.F. developed between the hot junction and the cold junction in ice. A suitable potentiometer for such work may be readily made or obtained from any of the standard instrument companies. The following gives the melting-points of a number of convenient metals :—

Metal	Melting-point
Zinc	419·0
Aluminium	657·0
Silver	961·5
Copper	1065·0

A curve showing the relation between E.M.F. developed and temperature can be readily obtained, and becomes a calibration curve from which any temperature within the range can be determined.

For industrial purposes there are portable galvanometers available, such as the galvanometer of Le Chatelier, which are calibrated, directly in degrees. The thermojunction itself is protected in a porcelain tube from the direct action of the furnace gases. This is very necessary, inasmuch as red-hot platinum very rapidly becomes contaminated by alloying with various metallic vapours or by coming in direct contact with impurities. Such contamination at once alters the thermoelectric properties, and causes grave errors. Convenient forms of the platinum-rhodium thermocouple are now supplied by nearly all the leading instrument makers. In order to keep the expense of the fire end as low as possible, the Bristol Company use the platinum and platimun-rhodium couple placed just at the end of the pyrometer tube, but further back, where the temperature is never supposed to exceed 1000°F., they substitute an alloy of inexpensive material of such thermoelectric properties that the resultant effect is as though the entire pyrometer were constructed of the more expensive material. Care must be taken to locate this junction of the inexpensive alloy and also the cold end.

For moderate temperatures iron and nickel have been used extensively in thermocouples. They have an advantage of being cheap and forming a couple of great sensitiveness. From ordinary temperatures up to about 800°F. or 1000°C. the iron-nickel thermocouple is serviceable. For industrial purposes this couple is offered in many forms. Thus the Bristol Company incloses it in an outer protecting tube of iron, which when burnt away may be discarded. Stansfield offers a simple modification consisting of a rod of nickel inclosed in a tube of iron, both metals fitting together at the end. The protecting tube furnishes one end of the junction. A water-cooled cold end completes a simple and effective pyrometer which may be read on any convenient millivoltmeter of approximately 25 mv. range.

The low cost of the Stansfield or the Bristol fire end, compared with furnace operation, would quite warrant a fresh end being used at each heating even were this necessary. There is no doubt of the ultimate deterioration of this couple after prolonged use, but this is not a serious objection owing to the low cost of renewals and the stout character of the fire end.

Recording instruments have been devised for the thermocouple, and many of them are extensively used in industrial work.

The first efforts to record automatically were made by Roberts-Austen, who employed the well-known photographic method. For research work involving rapid temperature changes the method has no equal. The small inertia of the moving system renders it quick to respond to the temperature fluctuations. A spot of light reflected from the mirror of a galvanometer falls on a moving photographic film. Subsequent development reveals the trace.

For industrial purposes various devices have been proposed. A simple one extensively used is to provide the moving galvanometer coil with an arm carrying a pen. This pen is raised slightly off a sheet of paper fastened to a revolving drum or disc. At regular intervals an arm depresses the pen and makes an ink dot, so that the position of the pointer on the scale is recorded by a series of these dots. The Bristol recording mechanism is essentially this, the dots occurring so rapidly, once every ten seconds, as to produce a practically continuous record. The Cambridge Scientific Instrument Company make a thread recorder, which consists of a suspended coil millivoltmeter in which the pointer is automatically depressed by clockwork every minute. This forces an inked thread on to a chart carried by a revolving drum. A similar recorder is sold by Baird and Tatlock.

The cold end, as a source of error in the general use of thermoelectric pyrometers, is often overlooked in the more inexpensive instruments. Many devices have been brought out for correcting the errors due to the cold end. A common one is to have the wires leading from the furnace carried down to the floor by a right-angled join. In this way a more uniform temperature is assured. A water-jacket seems to be quite satisfactory and simple to use. The Bristol Company, however, supply a 'cold end' compensator which consists of a pair of resistance wires in circuit with the thermojunction. A mercury column expands up a tube containing the wires, and thus short-circuits definite lengths. In this way, when the temperature of the cold junction rises and would produce a smaller reading by reducing the current, the rising mercury cuts out some resistance, and so maintains the current in the circuit at a constant value. *See* Fig. 2.

There are many ways in which the thermojunction is superior to other forms of electrical pyrometer. It is its own battery, requiring no auxiliary circuits. The fire ends are often cheap and easily replaced, and may be put a long distance away from the furnace. Both indicating and recording instruments may be attached to the same fire end.

Temperatures up to 1600°C. can be measured with simple reading instruments, although even with the platinum-rhodium couples for temperatures higher than 1200°C. continuous heating of the couple is not recommended.

Electrical Resistance Thermometer.

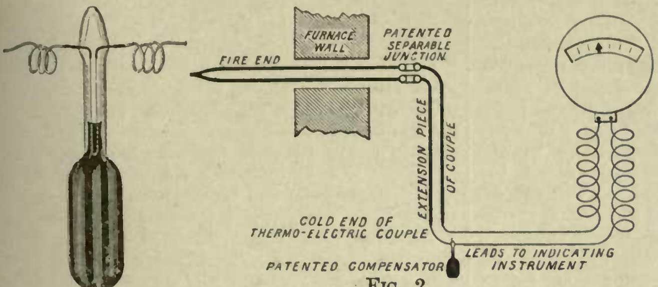

FURNACE WALL
PATENTED SEPARABLE JUNCTION
FIRE END
EXTENSION PIECE OF COUPLE
COLD END OF THERMO-ELECTRIC COUPLE
PATENTED COMPENSATOR
LEADS TO INDICATING INSTRUMENT

Fig. 2.

The measurement of temperature by the change in resistance of a platinum wire has been used for many years. The foundation upon which practically the whole of the modern methods rest is the classical work of Callendar in 1887 (Phil. Trans. 1887, A, 178). Not only were the various wires studied, but the simplest way to express the relation between air temperature and resistance changes was suggested. Callendar found that pure platinum was the best wire to use, and that coils of this metal wound on a mica frame would stand temperatures up to 1000°–1200°C. He suggested the platinum scale of temperature, which is given by

$$Pt=\frac{R-R_0}{R_{100}-R_0}\times 100,$$

as suitable and reliable for all samples of wire. The relation between the nitrogen thermometer and the platinum scale was given by the expression—

$$t-P_t=\delta\left[\left(\frac{t}{100}\right)^2-\frac{t}{100}\right]$$

where δ is a constant involving the two constants in the expression connecting the relation between resistance and the air scale. The value of δ for pure platinum wire is found to be 1·50. It changes with the purity a little, being as high as 1·7 for impure wire.

Platinum resistance thermometers are particularly valuable, inasmuch as the nitrogen scale, and through that the standard hydrogen scale can be absolutely defined. For the laboratory no other form of thermometer is so useful, no other thermometer so capable of such precision of reading over so wide a scale, from the lowest attainable temperature up to that of 1000°C. Beyond 1000°C. it is not safe to go. The minute disintegration of the platinum at that temperature very soon causes a change in the resistance of the fine wire coil, and so alters the readings.

There are two methods of reading platinum thermometers. The Wheatstone's bridge method with the compensated leads devised by Callendar, and the potentiometer method as used in Germany.

Of the two methods the former is much more practical. Figs. 3 and 4 illustrate the general plan of connections of the Wheatstone's bridge circuit. The first one shows a short bridge wire BW, with multiple coils r_1, r_2, r_3, &c., and the second shows one long bridge wire on which the whole temperature scale is placed.

The use of the compensated leads in the Wheatstone's bridge method, as shown at C in the diagrams, renders the indications of the thermometer independent of distance. Thus instruments for recording air temperatures have been operated up to a distance of nearly a mile with success.

In the Figs. R_1 and R_2 are ratio coils forming two of the arms of the bridge. B is the battery, G is the galvanometer. In Fig. 4, T is a telephone. In both figures the compensating leads are shown. A galvanometer detector is usually used as a null instrument for obtaining the balance-point, and hence the temperature; but a telephone can be conveniently substituted for the galvanometer without the use of an induction coil to interrupt the current, as in the pyrometer of Tory and Barnes. The make and break of a wire index, which acts as the balance-point finder on the bridge wire, causes the telephone to click at points other than the true balance-point. Callendar has devised a temperature indicator with a galvanometer the deflection of which is proportional to the temperature. This requires a specially connected differential galvanometer, and is not so practical as a null method with moving scale, as is illustrated in the Whipple temperature indicator, or the temperature indicators supplied by Leeds and Northrup in America.

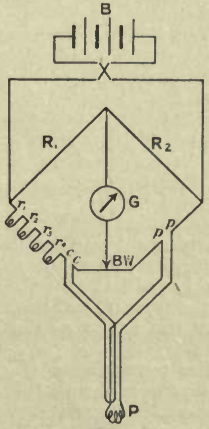


Fig. 3.

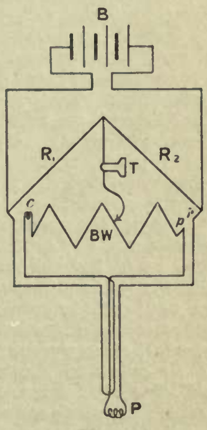


Fig. 4.

Resistance thermometers lend themselves readily to automatic recording. Such a recorder was devised by Callendar, and is supplied for industrial purposes (*see* Fig. 5). No temperature recording mechanism compares with it for flexibility and accuracy, but it is much less simple than the automatic recorders for thermojunctions. The Cambridge Scientific Instrument Company have perfected the instrument, and now supply it for all classes of temperature work. It consists essentially of an automatic Wheatstone's bridge or potentiometer, as the case may be. A galvanometer

G is provided with a special arm *a*, carrying double contacts *dc*, which straddle a contact wheel operated by clockwork C. A right and left-hand relay device, m_2 and m_1, connected with a differential gear, is governed by the double contact. A galvanometer potential sliding contact, SC, is moved over the bridge wire, BW, either to the right or left, as determined by the small swing of the galvanometer engaging one or the other of the double contacts on the contact wheel. The balance is determined by the contact point being moved automatically to the null position by the relay mechanism. Changes of temperature in the pyrometer, P, upset the balance, cause the galvanometer, G, to deflect and the contact, SC, to be moved to a new position of rest. A record is traced on a revolving drum, RD, by a pen attached to the galvanometer contact, SC. The Wheatstone's bridge connections are shown in Fig. 5, where R_1 and R_2 are the ratio coils, r_1, r_2, r_3, &c., are the multiple coils for the bridge wire. B is the operating battery. *cl* are the compensating leads. *pl* are the pyrometer leads. S_1, S_2, and S_3 are wheels engaging the thread for operating the sliding contact. GW is the galvanometer wire.

While requiring an external battery, platinum thermometers are independent of applied voltage, provided the current through the platinum wire is not large enough to seriously heat the coil. It is often a problem in commercial instruments to obtain sensitiveness with minimum current heating. No satisfactory metal has been found to replace platinum for high temperatures, and hence the fire ends are more expensive than the usual thermoelectric pyrometer.

Optical pyrometers. For the measurement of very high temperatures the only satisfactory pyrometers so far devised are the optical pyrometers. They are of two classes: those that depend on colour estimation, such as is illustrated most widely in industrial work by the Wanner, and those that depend on the measurement of the total radiation, such as the Féry pyrometer.

Optical instruments are coming rapidly into general use, and extend in range from a low red heat up to the highest attainable temperature. Their great advantage lies in the fact that they are used entirely outside the furnace, and hence suffer no deterioration by the excessive heat, as do all other pyrometers.

In order to obtain the temperature of a radiating body it is necessary to realise that the radiation depends not only upon the temperature, but also upon the emissive power of the radiating body. Of all bodies the radiation and absorption of a black body is the simplest possible, and is taken as the standard. For each temperature and wave length it emits the maximum possible amount of radiation, and it absorbs all the incident energy. For practical purposes a uniformly heated inclosure from which the radiation escapes through a small opening represents most perfectly the conditions of a perfect black body. In such 'black body radiation' it was shown by Stefan, and proved theoretically by Boltzmann, that the total radiant energy was proportional to the fourth power of the absolute temperature, or

$$\int_0^\infty E_\lambda d\lambda = aT^4$$

where E_λ is the energy corresponding to the wave length λ, and the integration includes all wave lengths, and *a* is a constant. It was shown by Wien that there was a maximum wave length corresponding to each temperature, and that the wave lengths including the maximum were displaced towards the visible region with rising temperature according to a simple law known as Wien's law—

$$\lambda_{max}T = C_1,$$

where C_1 is a constant.

Wien also showed that the energy corresponding with the maximum wave length was proportional to the fifth power of the absolute temperature, or $E_{max}\lambda^{-5} = C_2$, where C_2 is a constant. The most complete general equation connecting the energy of any particular wave length with the wave length and temperature has been given by Plank—

$$E_\lambda = C\cdot\frac{\lambda^{-5}}{e^{\frac{c}{\lambda T}}-1}$$

Wien also gives one, *i.e.*—

$$E_\lambda = C\cdot\lambda^{-5}\cdot e^{-\frac{c}{\lambda T}}$$

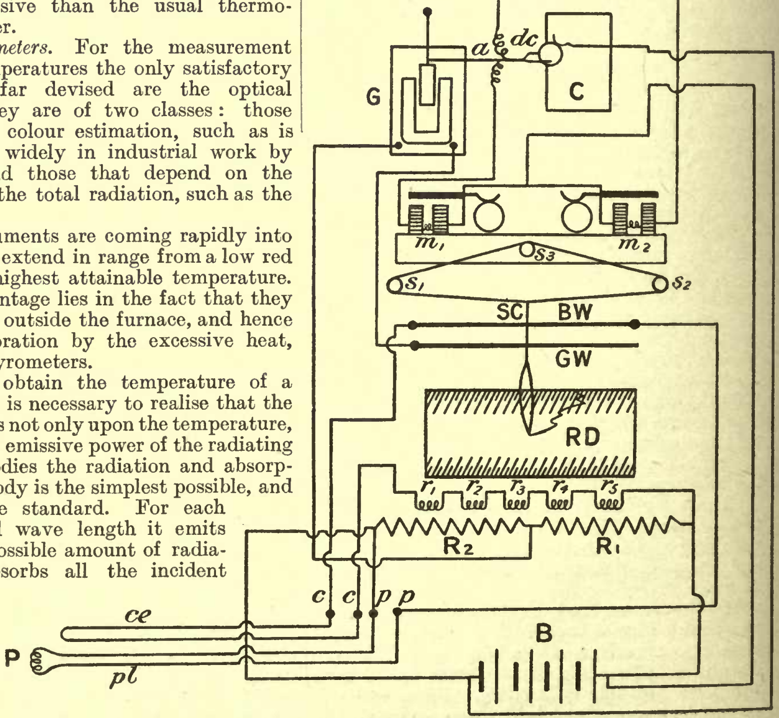


FIG. 5.

which corresponds to shorter wave lengths in the visible region. From this formula we may write—

$$\log E = K_1 + K_2 \cdot \frac{1}{\tau}$$

where K_1 and K_2 are constants, which gives a linear relation between the energy corresponding to any particular wave length and the absolute temperature.

The simplicity of this relation is the basis for calibration of pyrometers making use of the variation of the intensity of some particular wave length, usually a narrow strip in the red, with temperature. Determinations at two temperatures are sufficient to calibrate such a pyrometer.

Inasmuch as all bodies do not radiate as a black body, an optical pyrometer, calibrated from observations made on a black body, does not read correctly when estimating the temperature of all bodies. The error is not serious, however, for the reason that most bodies are viewed from the interior of a furnace whose sides are usually uniform in temperature with that of the body. In such cases the bodies do not deviate to any appreciable extent from that of a black body.

Polished platinum departs from a black body as much as almost any substance. At 1500°C. the intensity of the light emitted by this substance is only equal to that emitted by a black body at 1375°C. Hence, when viewed in the open by an optical pyrometer measuring the intensity of the red rays, it would appear to be 1375°C., when it was really at the higher temperature. This is expressed by saying that its 'black body' temperature is 1375°C. When this is viewed from the interior of a furnace at 1500°C., polished platinum reflects the equivalent amount of the light which it fails to emit at that temperature as a black body, and in consequence its temperature is measured correctly. Iron fortunately departs to a smaller extent from a black body, and an error of only 30°C. at 1000°C. is made by viewing iron in the open. For many years close estimates have been made by experienced observers of the temperature of a furnace by the eye. The enormous increase in the intensity of light with rise in temperature has made this possible. Thus if the intensity of the red light emitted by a body at 1000°C. be 1, then the intensity at 1500° will be 130 times as great and at 2000° over 21,000 times as great. At about 727°C. the intensity of the light increases 25 times as fast as the temperature. While trained workmen have gained great facility in estimating temperatures, owing to this fact, no accurate gauging of the temperature of a furnace can be made in this way. The eye is too much influenced by surrounding light and the state of health, to be relied on for uniform results.

Becquerel, in 1862, was the first to use the photometric measurement of the intensity of light as the basis for a system of pyrometry. He compared the red light emitted by a glowing body with that from a standard lamp. The measurement consisted in adjusting the light from the furnace entering the pyrometer until it was equal in intensity with that from a standard light. This is done in the well-known optical pyrometer devised by Le Chatelier (Compt. rend. 1892, 114, 214, 470) by means of an iris diaphragm. The rotation of the diaphragm to reduce or increase the light from the furnace gives the necessary scale for estimating the temperature. In the Wanner pyrometer (Phys. Zeit. 1902, 3, 112; Iron Age, 1904, 18, 24) a polarising devise is used for the same purpose. In the pyrometers of Holborn (Ann. Physik. 1903, 10, 225) in Germany, and Morse (Am. Machinist, 1903) in America, the adjustable scale is supplied not by varying the light from the furnace, but by varying the brilliancy of the electric comparison lamp. The filament of the glow lamp is placed in the field of view of the orifice of the furnace, and the electric current is adjusted until the glowing filament disappears. An ammeter A in series with the lamp and rheostat L supplies the scale for computing the temperature (*see* Fig. 6). In all these instruments calibration at two temperatures is sufficient in accordance with the law of Wien.

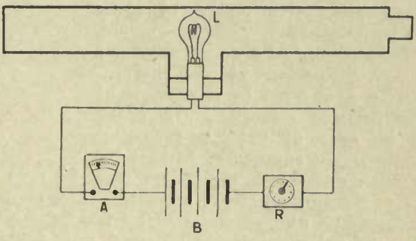


FIG. 6.

A very compact form of the Wanner optical pyrometer for lower temperatures has been devised, and is sold by Townson and Mercer. This extends in scale from 625°C. to 1000°C. The ordinary form of Wanner extends from 900°C. to 4000°C., smoked glass being used for temperatures above 2000°. For the standardisation of a pyrometer the amyl acetate lamp, as used in photometry, is employed. The comparison lamp of the pyrometer is adjusted to read correctly when the pyrometer is set to view the amyl acetate flame. Pyrometers

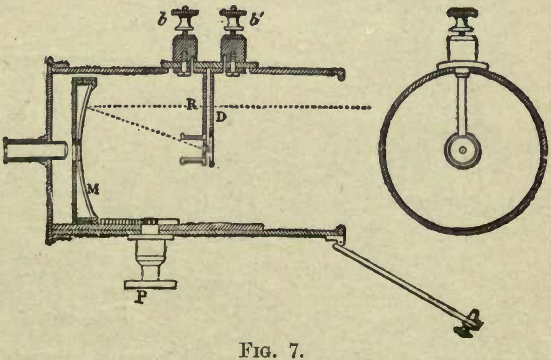


FIG. 7.

which are based on Stefan's law of total radiation have been devised by Féry. The best-known is his thermoelectric telescope. In the older type of instrument the rays from a furnace are focussed by a fluorite or large glass lens through a constant aperture on to a small copper-constantan thermoelectric couple. The rise in temperature of the couple is indicated by a galvanometer or millivoltmeter in the usual way. The industrial form of instrument was supplied with a large glass lens in order to offset the large absorptive power of glass for long heat rays. The instrument is independent of distance provided the entire surface of the thermocouple is covered by the image of the furnace radiation. In order to be sure of this, a focussing arrangement is supplied so that by adjusting the lens the image may be seen to cover the surface of the junction. The modern instruments as now supplied by the Cambridge Scientific Instrument Company are without the lens; a concave mirror at the back of the telescope tube focusses the rays upon the thermojunction (*see* Fig. 7). This is much more accurate, and avoids the selective absorption of the glass. In range the instrument is supplied to read from 500° to 1100°C., 600° to 1400°C., or 800° to 1700°C.; but it may be applied to higher temperatures by using suitable glass absorbing screens.

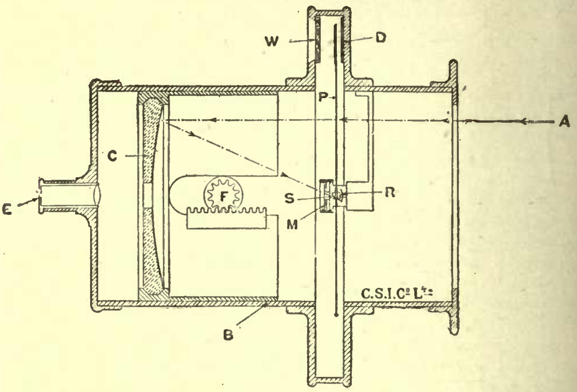


Fig. 8.

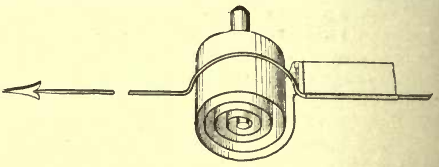


Fig. 9.

A recording instrument may be attached to the thermocouple similar in design to those supplied for thermoelectric pyrometers. This is the only optical pyrometer arranged with a continuous recording device. A simpler radiation pyrometer has been devised by Féry, and is similar in design to the thermoelectric telescope. The radiation is, however, focussed on to a small bimetallic spiral instead of the thermojunction (*see* Figs. 9 and 8). A pointer, P, attached to the spiral S moves over a scale, D, calibrated directly in degrees. A focussing arrangement, F, is necessary to ensure the complete covering of the spiral by the image. Thus the instrument is rendered independent of distance. The spiral is very small, measuring only 3 mm. in diameter and 2 mm. wide. This pyrometer is made in three ranges corresponding to those of the thermoelectric telescope, but it is not regarded as so accurate an instrument as the thermoelectric telescope.

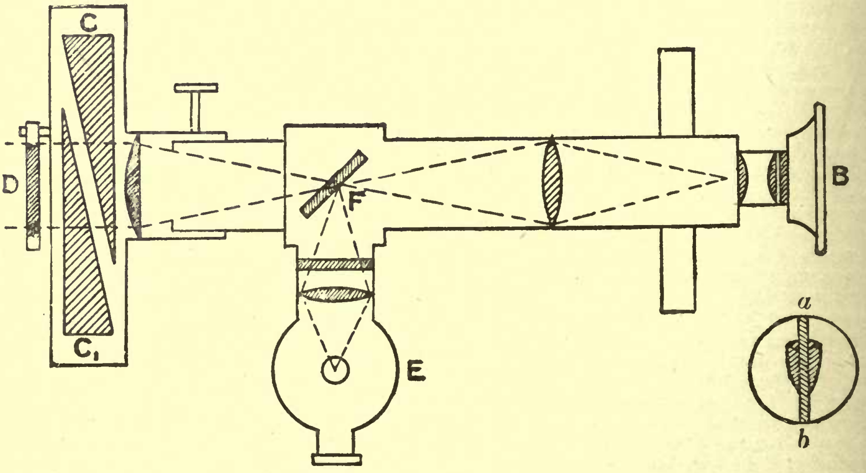


Fig. 10.

There are a number of optical pyrometers met with which are of more or less local importance, but they are all based on the fundamental principles set forth in the description of the forms already discussed. Thus the Féry absorption pyrometer (Figs. 10 and 11) is similar in principle to the Le Chatelier photometric pyrometer, except in place of the iris diaphragm for diminishing the light from the furnace two absorbing glass wedges C and C_1 are used. The slipping of the wedges over one another gives a sliding scale of an absorbing medium for reducing the light and estimating the temperature.

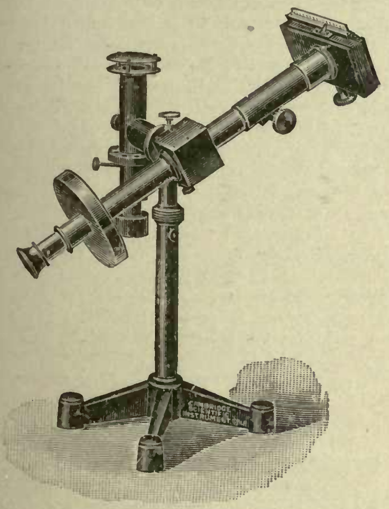


FIG. 11.

In Mesure and Nouel's pyrometric telescope the light is polarised by passing through a Nichol's prism. The light is then passed through a quartz plate cut so as to cause a rotation of the plane of polarisation. A second Nichol serves as analyser. The field of view is coloured because the rotation is inversely proportional to the square of the wave length. The angle between the two Nichols determines the colour that will be seen. A lemon-yellow colour is taken as being the most sensitive hue to the eye. A change in temperature causes a change in the composition of the incident light, and hence a change in the colour. By setting to the sensitive hue a scale of temperatures may be established.

Of the large number of pyrometers now offered for industrial work there are certain distinct uses for the various classes into which we have divided the present discussion. The selection of such an instrument must be left to the judgment and disposition of the man in charge of the work. Nearly all pyrometers give trustworthy results when carefully and intelligently used, and the best pyrometers are useless in careless and ignorant hands. So much is saved by economic furnace operation that too much care cannot be taken in the selection of a suitable pyrometer, but it must be understood that a pyrometer alone will not serve without the brains to operate and the judgment to interpret.

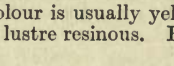
Bibliography.—Le Chatelier's High Temperature Measurements, translated by Burgess and published by Wiley and Sons, New York; A. Humboldt Sexton's Fuel and Refractory Materials, Van Nostrand and Co.; C. W. Waidner's Methods of Pyrometry; Waidner and Burgess' Optical Pyrometry; A. L. Day and E. E. van Nostrand's Measurement of Extreme Temperatures; the report of the Committee of the Iron and Steel Institute on Pyrometers suitable for Metallurgical work; and many other papers. H. T. B.

PYROMORPHITE. A mineral consisting of lead chloro-phosphate $(PbCl)Pb_4(PO_4)_3$ or $3Pb_3(PO_4)_2PbCl_2$, crystallising in the hexagonal system and isomorphous with apatite. It is occasionally found in sufficient quantity to be mined as an ore of lead (Pb 76·3 p.c.). The lead may be in part isomorphously replaced by calcium, as in the varieties polysphaerite, miesite, &c.; and arsenic may take the place of phosphorus, thus forming a gradual passage into the chloro-arsenate or mimetite. The two minerals pyromorphite and mimetite are very similar in appearance, and were formerly included together under the old names 'green lead-ore' and 'brown lead-ore' (Ger. Grünbleierz and Braunbleierz). The name pyromorphite has reference to the fact that fused globules of the mineral on solidification become bounded by a number of minute facets. The mineral usually occurs crystallised; the hexagonal prisms are often somewhat rounded and confusedly aggregated. The colour is usually yellow, brown, or green, and the lustre resinous. Hardness $3\frac{1}{2}$–4; sp.gr. 6·5–7·1.

Pyromorphite is a mineral of secondary origin, and is found, often in association with cerussite, in the upper oxidised regions of veins of lead ore. It has been obtained in many lead mines, perhaps most abundantly in the Friedrichssegen mine, near Ems in Nassau, where in 1868 a crystallised mass measuring 4×3×1 metres was found. Large quantities have also been yielded by the old mines of Huelgoat and Poullaouen in Brittany. It is common at Broken Hill in New South Wales and at Broken Hill in North-Western Rhodesia. L. J. S.

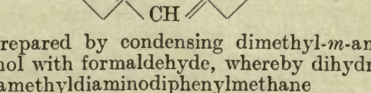
PYRONE DYESTUFFS. This name has been applied to certain members of the rhodamine series (*v.* TRIPHENYLMETHANE COLOURING MATTERS).

PYRONINE COLOURING MATTERS. The pyronines contain the pyronine ring

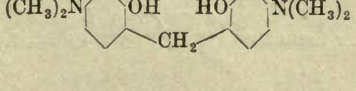


and are derivatives of diphenylmethane. They are obtained by condensing dialkyl-*m*-aminophenols with aliphatic aldehydes or acids, and are bluish-red, fluorescent, basic dyestuffs. They are dyed on cotton mordanted with tannin and antimony and on silk in a neutral soap bath.

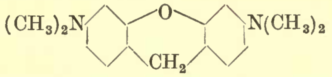
Pyronine G



is prepared by condensing dimethyl-*m*-aminophenol with formaldehyde, whereby dihydroxytetramethyldiaminodiphenylmethane



is produced; by treatment with sulphuric acid this loses water forming tetramethyldiaminodiphenylmethane oxide



which on oxidation furnishes the dyestuff. It forms greenish crystals soluble in water or alcohol with a red colour and yellow fluorescence, and dyes a brilliant bluish-red shade (Eng. Pats. 8673 and 13217 of 1889; 18606 of 1891; D. R. PP. 54190, 58955, 59003, 63081; Amer. Pat. 445684; Fr. Pat. 200401).

Pyronine B is a slightly bluer dyestuff, which is prepared in a similar manner from diethyl-*m*-aminophenol.

Acridine red 3 B is obtained by oxidising pyronine G; it dyes in shades slightly yellower than those given by pyronine (Eng. Pat. 1231 of 1892; D. R. P. 65282).

Literature.—See also Biehringer (Ber. 1894, 27, 3299; J. pr. Chem. 1896, [ii.] 54, 217). *V.* TRIPHENYLMETHANE COLOURING MATTERS.

J. C. C.

PYROPE *v.* GARNET.

PYROPHANITE. A manganese titanate $MnTiO_3$, found by Hamberg embedded in calcite occurring in the Harstig mine, Pajsberg, Sweden. Crystals belong to the rhombohedral-hexagonal system, and are isomorphous with titanic iron ore $FeTiO_3$; brilliant metallic lustre and deep red tint; powder, yellow with slight tinge of green; sp.gr. 4·537.

PYROPHORUS (from the Gk. πῦρ, fire; and φέρω, I bear) is a word which denotes in its widest sense any substance capable of taking fire spontaneously or on very slight elevation of temperature, as is the case with phosphorus, phosphoretted hydrogen, cacodyl, &c. If iron, cobalt, or nickel be reduced by hydrogen from their oxides at a low red heat, the metal is obtained in such a fine state of division as to become incandescent by the oxidising action of the atmosphere; this rapid oxidation is facilitated by the interposition of some infusible material, as alumina or magnesia, between the particles of oxide. When lead tartrate is heated in a glass tube, the lead is left in a very fine state of division, so that if the tube be hermetically sealed, then allowed to cool, the finely-divided particles of lead will take fire immediately on coming in contact with the air when the tube is opened. The reason of this is that the ratio of the surface exposed, when in a fine state of division, to the mass to be heated is so great that the oxidation of the exposed surface is sufficient to bring the mass to incandescence. The sulphides of potassium, sodium, and lithium, obtained by igniting the corresponding sulphates with lampblack in a covered crucible, are left in a finely-divided state, mixed with charcoal, and burn spontaneously on exposure to air. Homberg's pyrophorous is obtained by heating alum with lampblack, starch, or flour.

PYROPHYLLITE. Hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$, occurring either as pearly folia or as compact masses. In its low degree of hardness (H.=1–2), sp.gr. of 2·8–2·9, greasy feel, and general appearance it is strikingly similar to the two corresponding varieties of the mineral talc (*q.v.*, hydrated magnesium silicate $H_2Mg_3Si_4O_{12}$), and, furthermore, it has the same practical applications. In the foliated variety, usually of a pale green colour, the folia possess a perfect cleavage and pronounced pearly lustre, and they are arranged in characteristic fan-like or spherical groups. The compact variety, usually of a greyish or reddish colour, is included with other minerals of similar appearance under the general term agalmatolite (*q.v.*). Compact pyrophyllite sometimes forms large beds, and is quarried for slate pencils and tailors' chalk ('French chalk'), and by the Chinese for small decorative carvings. In the Deep River region, in Moore and Chatham Counties, North Carolina, it forms a bed in slaty rocks with a maximum thickness of 500 feet and extending for a distance of upwards of 6 miles. Large deposits of a similar character are also known in South Carolina and Georgia. On the talc and pyrophyllite deposits of North Carolina, *see* J. H. Pratt (N. C. Geol. Survey, Econ. paper No. 3, 1900), who gives the following analysis: I., yellowish-white, flaky pyrophyllite; II., apple-green pyrophyllite (also traces of CaO, MgO, K_2O in both analyses)—

	SiO_2	Al_2O_3	FeO	Na_2O	H_2O	Total
I.	64·53	29·40	0·67	0·28	5·45	100·33
II.	63·50	28·73	0·84	0·37	5·85	99·29

L. J. S.

PYRORACEMIC ACID *v.* PYRUVIC ACID.

PYRORETIN *v.* RESINS.

PYROSINE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

PYROTARTARIC ACID, and α- and β-*iso*-**PYROTARTARIC ACIDS** *v.* GLUTARIC ACID.

PYROTECHNY. The art of making fireworks. Although formerly applied to the smelting and roasting of metallic ores, and to other metallurgical processes involving the use of fire, the term 'pyrotechny' has become narrowed down in modern times so as to include only those effects of fire that are produced mainly for scenic displays. That mixtures of certain substances, some of them more or less familiar, when ignited were capable of producing brilliant and startling effects was known to the early ancients. The art of preparing such mixtures, and of manipulating their mode of combustion, had arrived at a considerable degree of perfection long before the true nature of even the commonest of the materials was known, and before the true principles underlying their use were in the least understood. For these reasons it is that the art of pyrotechny, more perhaps than any other art carried on at the present day, is conducted so largely by 'rule of thumb.'

Pyrotechny is said to have had its origin in the East, firework displays being well known in China for many centuries prior to their introduction into Europe, and even to this day the Chinese and Japanese excel in the production of certain fireworks of great beauty. In Europe pyrotechny was first practised by the Florentines, towards the end of the thirteenth century, at the time that the knowledge of gunpowder began to be diffused among the Western peoples; from Italy the art spread to France, and thence to England and Germany.

Pyrotechny is essentially a 'handicraft'; that is to say, it is one of the very few remaining arts which is still carried on entirely by hand,

and which has not been invaded and revolutionised by the introduction of modern machinery. Even in the largest factory in this country machinery is only employed for woodworking, paper-cutting, and similar operations, and not in the actual making of the fireworks.

Notwithstanding the great variety of effects produced by the many different kinds of fireworks, they all have certain fundamental essentials in common. All fireworks contain a combustible substance, and a supporter of combustion. The combustible, or the *fuel*, may be either one or more of a great variety of substances, such as sulphur, carbon, shellac, resin, pitch, starch, sugar, lycopodium, various picrates, particularly the potassium and ammonium salts; various sulphides, as those of iron, antimony, arsenic; various metals, as iron, antimony, zinc, copper, magnesium, and aluminium.

The supporters of combustion are mainly certain oxygen salts, such as chlorates and nitrates, which are readily able to give up their supply of oxygen to the combustible bodies. The pyrotechnist seldom supplies the fuel with a sufficient amount of the oxygen salt to bring about the complete combustion of the former. The object of the firework-maker is not to discharge into the air the completely oxidised products of combustion, but rather to throw out a certain quantity of material which is in a condition to enter into active combination with the oxygen of the air and to carry on its combustion at the expense of this outside supply of oxygen, many of the combustible substances thus emitted being among the products of the complex chemical reactions which are going forward at the time.

The exact nature of the chemical changes which accompany the burning of a firework are little known. The various mixtures, therefore, which are used to produce certain results have, in most cases, been arrived at, not by processes of scientific reasoning, but by purely empirical rules. Although the art of pyrotechny is regarded as a chemical one, it embraces many mechanical considerations and details which are of no less importance to the production of scenic displays than those which are more distinctly chemical.

For convenience the subject may be subdivided as follows:

1. Preparation of mixtures.
2. Manufacture of cases.
3. Loading of cases.
4. Various accessories, as quick-match, touch-paper, leaders, port-fires.

1. The mixtures used in pyrotechny are called compositions or fuses, and their preparation requires some care. In this branch of the work a knowledge of chemistry is of the greatest importance to the pyrotechnist, in order that he may not only get the best results out of his materials, but also that he may avoid the dangers which attend the use of the highly explosive combinations he has to deal with. Many mixtures also are liable to undergo chemical decomposition, so that they can only be employed when the firework is to be used within a short time of its manufacture. Other mixtures are liable to more rapid spontaneous decomposition, resulting in the ignition and explosion of the materials.

In former days most mixtures were more complex, containing more ingredients than those used at the present time; particularly is this the case with mixtures for coloured effects. This is doubtless due chiefly to the greater purity of modern chemicals, for it is well known that a strontium salt, for example, which contains any quantity of a sodium salt with it will have the crimson colour it imparts to a flame more or less completely masked by the yellow of the sodium. In fact, the purity of the substances used is a point of the highest importance.

The staple materials employed in a great number of fuses are potassium nitrate (known as 'petre'), sulphur, charcoal ('coal'), and meal powder ('meal'). The addition of either 'petre' or 'meal' to a fuse has the effect of making it quicker, whilst the addition of sulphur slackens it; *e.g.* quick-match made from meal, 6 parts; sulphur, 1 part, burns with the greatest violence; whilst that made from meal, 1 part, and sulphur, 1 part, will scarcely burn at all.

The nitre used is always in the form of meal. The sulphur should be crushed lump in preference to flowers; in either case it must be carefully washed free from acid and dried. Most manufacturers avoid the use of 'chemical charcoal,' as it is termed—*i.e.* charcoal which has been made by distillation in retorts for the manufacture of pyroligneous acid. The weighed materials are thrown upon a table, rolled down with a wooden roller exactly resembling a cook's rolling-pin, and thoroughly mixed by being sifted together through sieves. Every pyrotechnist has his own particular formulæ, which are usually kept more or less as trade secrets; the variety of mixtures which are used for the same firework will be seen from the following instances:—

Rockets.

Sulphur . . .	8	1	1	2	4	2	4	8	4	12	1	1
Charcoal . .	27	2	2	12	8	4	7	11	5	17	2	4
Nitre . . .	36	4	4	20	16	9	16	32	16	50	5	8
Meal powder .	6	2	1	1	3	—	—	—	—	—	—	—

Roman candles.

Sulphur . . .	1	2	2	3	3	4	4	7
Charcoal . . .	2	3	3	3	1	1	3	8
Nitre	4	2	9	8	4	5	8	21
Meal powder . .	3	8	4	3	5	4	8	12

Tourbillons.

Sulphur	1	3	3	7	3	4	4	2	4
Nitre	4	16	5	10	8	17	17	4	8
Charcoal	2	8	3	4	3	4	5	—	—
Meal powder . . .	1	8	11	24	16	—	—	4	9
Steel filings	—	—	—	8	6	—	—	—	—
Cast-iron borings . .	—	—	—	—	—	6	8	3	4

It is in the preparation of mixtures for colour effects that the purity of the chemicals is of the greatest importance. Coloured stars for shells, Roman candles, rockets, &c., consist of small compacted masses of composition; they are called 'cut' or 'naked' stars, and 'pill-box' stars, according to the method of their manufacture. 'Naked' stars are made by moistening the composition with a solution of either gum, shellac, or with starch, spreading it out upon a slab with a spatula, and marking the surface by cross parallel lines into small squares. When nearly dry, it is broken up by the marks, and exposed until dry. The rough edges obtained by this method enable the star to ignite readily. Stars made in this way must contain nitre as the oxygen supply, and not potassium chlorate; for although chlorate mixtures burn more fiercely, they are more difficult to ignite.

The following formulæ are for constructing 'naked' stars, known as 'comet' or 'tailed' stars:—

Sulphur . .	5	24	2	—	1	2
Nitre . . .	5	24	9	—	10	20
Charcoal . .	2	8	2	3	6	12
Vegetable black .	1	3	3	6	—	—
Meal powder .	8	30	6	16	5	7

'Pill-box' stars are made by compressing the dry composition into short cylinders of paper, and inclosing a piece of quick-match for their ignition. These all contain chlorates, as will be seen by the formulæ shown in next column.

—	Blue stars with sugar					Blue stars without sugar					
Potassium chlorate .	8	36	40	6	40	5	40	6	8	2	5
Calomel . . .	4	18	24	5	—	4	20	2	2	—	—
Sugar . . .	5	12	12	4	9	—	—	—	—	—	—
Copper sulphide .	3	22	12	—	22	4	20	—	2	—	1
Stearin . . .	—	1	1	—	2	—	—	—	—	—	—
Oxychloride of copper .	—	—	3	—	—	—	2	—	—	1	1
Ammonium chloride .	—	—	—	—	6	—	—	—	—	—	—
Copper filings . .	—	—	—	1	—	—	—	—	—	—	—
Shellac . . .	—	—	—	—	—	1	5	—	—	—	—
Sulphur . . .	—	—	—	—	—	—	—	3	4	1	2
Copper oxide . .	—	—	—	—	—	—	—	1	1	—	—

The use of copper chlorate is practically inadmissible, on account of its deliquescence, as well as its danger. The well-known substitute (obtained by dissolving copper sulphate and potassium chlorate together in water, evaporating to dryness, moistening with ammonia and again drying), called Chertier's copper, although yielding excellent blues, is practically abandoned by manufacturers on account of its liability to explode.

The following formulæ may be used for red, green, and yellow stars:—

—	Red				Green					Yellow			
Potassium chlorate . .	16	8	16	28	16	8	1	—	6	8	4	12	4
Sulphur	5	6	—	—	5	7	1	1	—	—	—	—	1
Charcoal	1	1	—	—	1	1	—	—	—	—	—	—	—
Calomel	—	—	—	12	—	—	—	—	5	—	—	—	—
Shellac	—	1	—	—	—	2	—	—	—	2	1	3	—
Sugar	—	—	7	12	—	—	—	—	5	—	—	—	—
Strontium nitrate . . .	16	16	—	—	—	—	—	—	—	—	—	—	—
Strontium carbonate . .	—	—	11	5	—	—	—	—	—	—	—	—	—
Barium nitrate . . .	—	—	—	—	16	21	—	—	7	—	—	—	—
Barium chlorate . . .	—	—	—	—	—	3	2	4	3	—	—	—	—
Sodium oxalate . . .	—	—	—	—	—	—	—	—	—	3	2	8	1

Coloured mixtures are sometimes made up with magnesium filings, to produce specially brilliant stars and asteroids. These vary only slightly from the above formulæ, with the addition of magnesium filings; one illustration of each for red, green, blue, yellow, and white may be quoted. For other coloured fires, *see* BENGAL LIGHTS.

—	Red	Green	Blue	Yellow	White
Potassium chlorate	2	—	5	4	—
Sulphur . .	2	1	2	—	4
Charcoal . .	1	—	—	—	—
Shellac . .	—	3	1	1	—
Calomel . .	—	—	2	—	—
Magnesium filings .	2	2	2	1	2
Strontium nitrate .	8	—	—	—	—
Barium chlorate .	—	12	—	—	—
Copper oxychloride	—	—	2	—	—
Sodium oxalate .	—	—	—	2	—
Potassium nitrate .	—	—	—	—	12
Antimony sulphide	—	—	—	—	1

Of late years the metal aluminium in fine powder is largely used either in conjunction with magnesium or as a substitute for it in the above mixtures. Some of these aluminium mixtures have been made the subject of patents, whilst many others are more or less trade secrets. Thus powdered magnesium or aluminium (or mixtures of these metals in varying proportions) mixed with the peroxides of calcium, magnesium, or manganese, along with a suitable quantity of strontium nitrate, gives a very brilliant and rapid red fire. An explosive mixture known as 'Brockite,' patented and manufactured by Messrs. Brock, consists essentially of barium chlorate and aluminium powder. This mixture enters largely into the composition of many fireworks from shells down to the simple cracker. Modern smokeless gunpowder, guncotton, and other high explosives are not employed in pyrotechny.

2. *The manufacture of cases.* All cases are made of paper, and the selection of the paper is a point of some importance. The paper varies in quality and stoutness, according to the particular kind of firework to be made and to the amount of strain which will be put upon the case. In some instances the material of the paper influences the character of the display produced by a particular firework. For example, the Japanese 'spur fire,' which on burning throws scintillations of a peculiar beauty, owes this quality partly to the special paper of which the case is made, for if the same mixture be introduced into a case made of another paper it will be found to have lost to a large extent the property of throwing out these characteristic scintillations. Most of the papers used are of a superior quality, as it is found that greater

strength can be obtained by the use of a smaller quantity of good paper than by employing more of one of inferior quality; paper which is 'loaded' or adulterated cannot be used. The majority of cases are made of brown paper, although some, and more especially the smaller sorts, as crackers, Catherine wheels, &c., are always made of white cartridge. In a large factory several scores of different papers will be used. The paper is cut to the various sizes required by cutting machinery, and into certain special irregular shapes by dies.

Owing to the great variety in size required, the cases are all made by hand, and, but for slight variations, in the same manner. The tools employed are of the very simplest description, consisting of a wooden or metal roller called the 'former,' and a short wooden board with a handle on one side, known as the 'rolling board.' For the larger cases the paper is pasted over its whole surface, and rolled round the 'former,' the operation being done on a narrow slate table. The rolling board is then passed rapidly over it a few times with a firm steady pressure (Fig. 1).

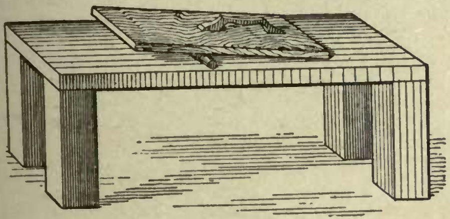


FIG. 1.

The former is then withdrawn, and the case stood on end until it is so far dry that it can be laid on its side without risk of its losing its cylindrical shape. It is then stacked in a bin in a chamber through which a current of warm air is circulating, in order to render it perfectly dry. In many fireworks the cases have to be partially closed, or constricted near to one end. This is technically known as 'choking.' It may be effected in two ways, either by compressing the walls of the case to the desired extent, or by partially filling the mouth of the case with clay. When the first of these plans is adopted, the operation is performed when the case is freshly made, and only partially dry. For small fireworks it is done by means of a hand lever, made of two blades of steel, and screwed to the edge of the table (Fig. 2).

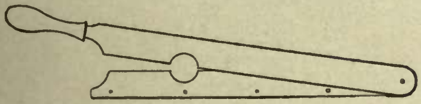


FIG. 2.

For larger cases a foot lever is employed. A noose of cord is looped round the case, one end being fastened to a hook in a wall, or upright post, while the other passes over a wheel to a lever upon the floor, which can be worked by the foot. As the cases have to be choked down to a certain definite orifice, a 'choking-pin' (Fig. 3) is inserted at the time the constriction is being made, which also secures another essential condition, viz. that the choke shall be central. The case is tied round the choke with a string suitable in thickness to the size case, and the whole is then allowed to dry.

When the constriction is effected by means of a clay plug, the operation is performed at the time of loading.

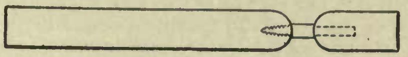


FIG. 3.

For small cases the paper is pasted only along the edges; the former, in this instance a thick metal wire, is placed nearly in the middle of the paper. One end is then folded over nearly to the other, and the double paper rolled over the former (Fig. 4).

The case may be closed at one end by folding the paper in upon the end of the former. These cases require no special drying. Light cases, such as these, are usually made by women, one operator being able to turn out many hundreds in an hour.

Besides cylindrical cases, there are cases made in the form of a sphere, known as 'shells.' These shells, which are constructed of various sizes, up to even 24 ins. in diameter, are made by a process technically known as the 'wet-broke' process. Brown paper of a specially good quality is thoroughly pasted on both sides; strips are then *torn* from the pasted length, and laid upon the inside of a hemispherical bowl or mould, the strips radiating upwards from the centre to the circumference, the ends lapping over the edge of the mould; the workman continues this process until the desired thickness of paper is obtained, which will vary according to the size of the shell from about ½ to 1 in. It is then removed from the mould and allowed to dry, when it presents the appearance shown in Fig. 5. These hemispheres are then placed in a lathe, and the ragged lips or rims carefully turned off. A good workman will so turn out these paper hemispheres that the cut edge shows a most beautiful and perfectly homogeneous section. Two of these hemispheres are securely glued together to form the complete shell. These shells are destined to carry coloured stars, and to be fired from a

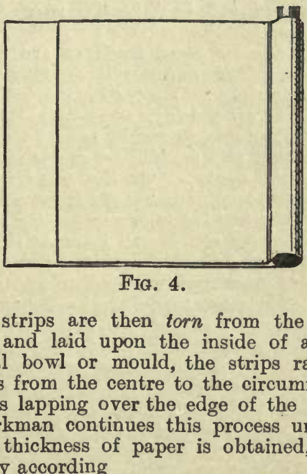


FIG. 4.

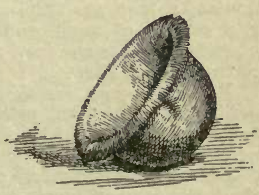


FIG. 5.

mortar; the mould in which they are made has therefore a slightly raised ridge running part of the way down from the circumference, and producing a corresponding indentation, or 'dimple' in the shell, which allows of room between the shell and the side of the mortar for communicating the fire to the propelling charge below.

3. *Loading the cases.* This operation varies in details according to the special firework to be filled, but, broadly speaking, it may be divided into two sections, viz. *loose-filling* and *ramming.* The apparatus employed in the first of these methods is a metal funnel, of an elongated shape, and a wire, the operation being known as 'wire and funnel' filling. The wire is usually square, and of such a thickness that it will just pass through the end of the funnel. The case to be filled, if a choked case, is placed upon a stand with its choked end fitted upon a nipple fixed for its reception; the nose of the funnel is then inserted into the open end of the case, and by drawing the wire quickly up and down the composition is driven uniformly into the case. When full to the required height, usually determined by a mark upon the wire, the case is closed up. With small fireworks (such as squibs, &c.) this is done by firmly squeezing the end of the case with a tool known as the 'closing-in' machine, and finally dipping the end into a composition, usually red in colour, and technically called 'dip.'

Glue and red lead is the most common mixture for 'dip.'

Long narrow cases (such as are used for crackers and Catherine wheels) are filled without the use of a stand. For the last-named of these fireworks no special tools are required, the long narrow tube being wound by hand upon a small wooden disc, and secured by strips of tape or paper glued across. In the manufacture of crackers two special pieces of apparatus are employed. The first is a rolling or flatting machine. The filled cases are passed between the rollers of this tool, and thereby squeezed flat, the pressure being carefully regulated to the required degree. The other tool is the bending machine. It consists of two upright rectangular brass pillars fastened to a base at such a distance apart as to allow of four of the flattened cases to lie abreast between them (Fig. 6). The cases are bent backward and forward over steel wires about the thickness of a stout steel knitting-needle, until the requisite number of bends is obtained; they are then pressed firmly down with a piece of wood, and removed from the machine. The wires drop out, and are ready for the next set of cases.

The bent cases are then tied up into the familiar compact form with a suitable thread, and the ends primed in the usual way with touch-paper.

Of the second method of loading cases, in which the composition is rammed in, two illustrations may be given, viz. the Roman candle, in which the mixture is gently rammed, and the rocket, in which it is 'malleted.' The case for a Roman candle is a straight or unchoked one. It is placed upon a block, called a 'settle,' the projecting core of which A (Fig. 7) exactly fits into the case.

A small quantity of finely-powdered and sifted clay is first introduced, and tightly driven down by means of the 'rammer,' a wooden rod, which loosely fits into the case. A few smart blows from a mallet upon the head of the rammer will compress the clay into a solid mass, which should occupy about ½ an inch up the case. Fine potters' clay is usually recommended, but London pyrotechnists use the common London clay. The use of plaster of Paris instead of clay has been introduced by the Americans, and is said to be much superior. The plaster is mixed with a little water until of about the consistency of soft putty; a pellet is moulded with the fingers, dropped into the case, and gently pressed by the rammer. The case is next to be filled with composition, and coloured stars, alternating. Each layer of mixture is introduced in two quantities, and rammed down by simply 'jumping' the rammer. If more force is applied the stars are liable to be crushed. Care is taken to regulate the charge of mixture, so that each star shall, as far as possible, be blown out to the same distance. Various devices are adopted to secure the ignition of the star, to prevent it becoming a 'blind star,' as it is termed, one being to make the stars with a hole in them, which is primed with a piece of quick-match.

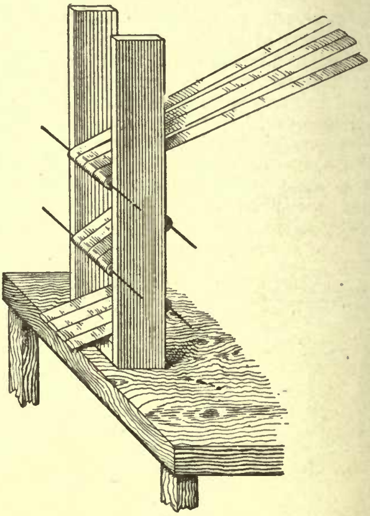


FIG. 6.

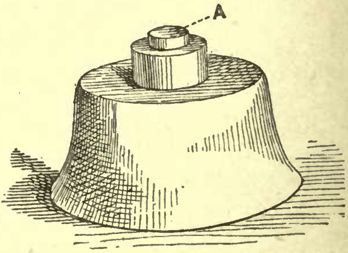


FIG. 7.

Rockets are loaded by the mixture being forcibly rammed into the case by a mallet, and as this firework is in some respects of a special construction, in which the exact relation of all the parts to one another has to be made with much nicety, its construction may be described at greater length. The rocket is a hollow firework, and therefore has to be constructed with special tools. (Very small rockets are often packed solid, and a hole bored up the inside with a common drill.) These consist of a steel conical spindle, or core, firmly screwed into a base of either hard wood or brass, the length and thickness of this spindle varying for each size rocket, a set of wooden rammers, or 'drifts,' of different lengths, and having a cylindrical hole bored nearly up to the head. The number of drifts required for each rocket depends also upon the size; for larger cases four are used. Formerly a 'mould' was employed; this was a strong wooden jacket, to surround the case during the loading operation, to prevent it from splitting; but this is never employed by the manufacturer to-day, owing to improvements in the case-making, resulting partly from the use of better paper. The case to be charged is placed upon the spindle, which must be stood upon a massive wooden or stone block to prevent vibration. It would be quite impossible, for instance, to load a rocket tightly if hammered on a wooden table or floor.

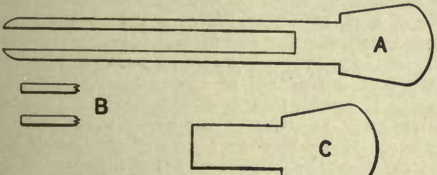


FIG. 8.

If the case has been previously choked by constriction a rammer (technically called the 'setting-down piece') is introduced, and driven down with a few sharp taps with a mallet: this is to smooth out any wrinkles in the choked end. This 'setting-down piece' A (Fig. 8) resembles the longest 'drift' in all respects except that the end of the latter is cut square, as shown at B, Fig. 8. To prevent the choke from becoming enlarged by being burnt away a small quantity of clay is introduced, and well 'malleted' in with the longest drift, the clay occupying the space shown at CC, Fig. 9. Except in the case of the largest rockets, most manufacturers prefer to use a straight case, and choke it at the time of loading by ramming in a layer of clay, straight cases being easier and cheaper to make than choked ones; with large rockets, however, there is some risk of the clay choke being blown out. Fig. 9, drawn to scale, shows such a case, with the clay choke and spindle. The composition is introduced into the case in 12 equal quantities, measured by a scoop made to hold the exact amount. Each scoopful is malleted well in, the workman being careful to give the same number of blows—usually 18 to 20—and of as nearly equal force as he can judge. As the load rises in the case a shorter 'drift,' with a smaller bore, is used. The length of the longest drift, which must be bored large enough to admit the spindle at x, will be 8 times the diameter of the case, exclusive of its head. When the composition reaches one-third up the spindle y (Fig. 9), which is known by a mark on the drift, the second drift is brought into use; the ramming is continued with No. 2 until the load reaches z (Fig. 9), again ascertained by a mark on the second drift. The third drift loads up to the top of the spindle, when the hollow drifts are replaced by a solid one, C (Fig. 8). The drifts diminish in length by 2 diameters of the case, the three hollow ones being respectively 8, 6, 4, while the solid one is 2 diameters, the 'setting-down' piece being the same length as the longest drift, but with a round end. The case is filled to within about 1 diameter of the top, and then a layer of clay is driven down. The case is removed from the spindle by a gentle twist or turn in one direction only. The nomenclature adopted by the manufacturers to denote various sizes in rockets is the old-fashioned and arbitrary one of 'pounds' and 'ounces'—these weights referring not to the weight of the rocket, but to the weight of a leaden ball of the same diameter as the mould formerly used for loading. As every maker varies in the thickness of his cases, this conveys no exact criterion of the real size of the rocket. By general consent, a case of $1\frac{1}{8}$-in. bore is called a 'pound' rocket, and a $\frac{1}{2}$-in. case an 'ounce' rocket. The following table gives, in a convenient form, the exact sizes of the various parts. The inside diameter is given in eighths of inches, and the relation which should subsist between this measurement and that of thickness of the case, length, and thickness of the stick, will be seen at a glance:—

Inside diameter in eighths	Outside diameter	Length of case in inches	Length of spindle	Diameter of bottom of spindle	Length of stick in inches	Thickness of stick
$\frac{3}{8}$	$\frac{4\frac{1}{2}}{8}$	3	$2\frac{1}{4}$	$\frac{3}{20}$	3×8=24	$\frac{1\frac{1}{2}}{8}\times\frac{1\frac{1}{2}}{8}$
$\frac{4}{8}$	$\frac{6}{8}$	4	3	$\frac{4}{20}$	4×8=32	$\frac{2}{8}\times\frac{2}{8}$
$\frac{5}{8}$	$\frac{7\frac{1}{2}}{8}$	5	$3\frac{3}{4}$	$\frac{5}{20}$	5×8=40	$\frac{2\frac{1}{2}}{8}\times\frac{2\frac{1}{2}}{8}$
$\frac{6}{8}$	$\frac{9}{8}$	6	$4\frac{1}{2}$	$\frac{6}{20}$	6×8=48	$\frac{3}{8}\times\frac{3}{8}$
$\frac{7}{8}$	$\frac{10\frac{1}{2}}{8}$	7	$5\frac{1}{4}$	$\frac{7}{20}$	7×8=56	$\frac{3\frac{1}{2}}{8}\times\frac{3\frac{1}{2}}{8}$
$\frac{8}{8}$	$\frac{12}{8}$	8	6	$\frac{8}{20}$	8×8=64	$\frac{4}{8}\times\frac{4}{8}$
$\frac{9}{8}$	$\frac{13\frac{1}{2}}{8}$	9	$6\frac{3}{4}$	$\frac{9}{20}$	9×8=72	$\frac{4\frac{1}{2}}{8}\times\frac{4\frac{1}{2}}{8}$
$\frac{10}{8}$	$\frac{15}{8}$	10	$7\frac{1}{2}$	$\frac{10}{20}$	10×8=80	$\frac{5}{8}\times\frac{5}{8}$

The stick may be attached to the rocket by being securely tied with string near to the two ends of the case. Modern manufacturers usually bind upon the rocket case a smaller case, just large enough to admit the end of the stick when it has been roughly rounded. Two short spikes are driven into this rounded part of the stick, which, on being thrust up into the case and twisted, cause it to hold very securely. A rocket when laid across the finger should just balance when the point of support is about an inch along the stick, away from the mouth of the case.

The weight of composition required to load a rocket may be found by the following formula, where d=internal diameter of case in eighths of inches:—

$$\frac{d^3}{9}=\text{number of drachms.}$$

e.g. the charge for a $\frac{9}{8}$ (so-called 'pound' rocket) $=\frac{9^3}{9}=81$ drachms $=5$ ozs. 1 dr.

Rockets are always made to carry up a load of various combustibles; these are contained in a slight paper case, known as the 'pot,' which is glued to the head of the rocket. This pot is to be burst, and its ignited contents thrown out, at the moment the rocket reaches the top of its flight, and before it has turned over. The bursting of the pot and the inflammation of its contents are secured by a small quantity of powder, known as 'bursting powder,' the weight of which is usually about $\frac{1}{9}$th the weight of the materials in the pot. This 'garniture' of a rocket may consist of a variety of things, such as gold or silver rain, coloured stars, magnesium stars, parachutes, whistling fireworks, &c.

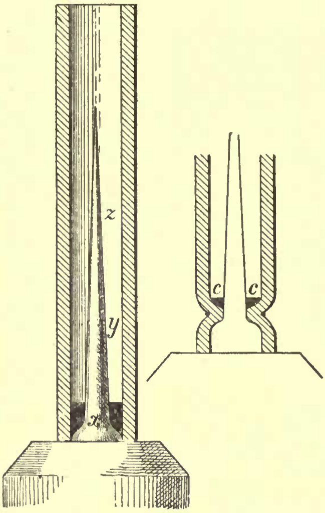


FIG. 9.

Rockets garnished with parachutes are called 'asteroid rockets.' The parachute is made of thin alpaca, silk, or tissue paper. The latter has to be strengthened by a thread of cotton round its edge, and the paper thoroughly softened by a process of crumpling, to insure the parachute opening when thrown out. Suspended by threads from the parachute is the case, loaded with coloured compositions, usually layers of different mixtures, so that the colour may change as the parachute sails along.

The whistling firework consists of a short paper case, closed at one end, and charged with a composition consisting of potassium picrate 3 parts and nitre 2 parts, or the picrate 15 parts mixed with asphaltum 1 part. The case is not choked, nor is the mouth shaped; but on ignition the outrushing flames and gas emit a shrill weird whistling sound, gradually rising in a 'crescendo' to a maximum loudness and then falling with a rapid diminuendo. Usually five of these are loaded into a 'pot' to garnish a rocket.

The weight of the load which a rocket can safely be made to carry is the same as that of the composition with which it is filled; thus a $\frac{9}{8}$ ('pound') rocket can be made to carry up a load of 5 ozs. 1 dr.

Of all the materials which can be used to garnish rockets, that which produces by far the most brilliant effect for the weight and cost is phosphorus; but the extreme danger attending the manipulation of this substance has prevented its use by pyrotechnists to any extent. Patents have been taken from time to time with a view to diminish or overcome this difficulty. One of these consists in packing the phosphorus, cut in short sticks of about 1 in., into a perforated paper cage, which has been previously dipped in melted paraffin wax. The cage, with its load, is immersed in a tin can of water until required. When the rocket is ready to be fired, one of these paper cages is taken, the excess of water drained off, and the cage introduced into the rocket pot, into which it just fits. On the bottom of the pot a layer of bursting powder has previously been placed, and covered over with a thin piece of waterproofed paper.

When the phosphorus is introduced the cone is fitted in and the rocket fired.

4. *Touch-paper* is made by impregnating a thin paper—by general consent, blue—with potassium nitrate. The paper commonly employed is 12-lb. double crown. The sheets are spread out and brushed over on one side only with a solution of nitre, containing 1 oz. of the salt to a pint of water. The paper is used for enveloping the live end of fireworks.

Slow-match is prepared by soaking blotting paper in a solution of lead nitrate. Blotting paper is brushed on both sides with a solution containing 2½ oz. of the nitrate to a pint of water. When dry six layers of the paper are pasted together and pressed flat, forming, when again dried, a stiff board. This is then cut into suitable strips with a sharp knife.

Quick-match is made by impregnating cotton with a mixture of starch paste and meal powder. Meal powder is stirred into hot thin starch paste until it has the consistency of paint and is quite smooth. Lamp cotton, with six or eight strands, is then coiled into the vessel containing the 'meal paste,' the cotton being pressed carefully down with a wooden stick to insure its being thoroughly soaked. It is then wound out on to wooden frames, usually about 6 feet high and 2½ feet wide; these frames are provided with pivots, so that they can be swung upon a support. The frame is turned slowly over and over by one workman, while a second feeds out the cotton through his hand, rounding the wet thread with his fingers as it passes. The frame is then laid down and meal powder sifted first on one side and then on the other; the cotton is then allowed to dry. When cut it ought to show a perfectly black section. It is preserved in long boxes, as it is necessary to guard it from getting cracked.

Leaders consist of thin paper tubes, through which quick-match is threaded, in order to convey fire rapidly from one firework to another. The tubes have to be such a size as to allow the match to be introduced without any forcible pushing. The more closely the match fits the pipe the more rapidly does the combustion propagate itself through the length. The pipes are made to any length by slightly pinching the end of one piece and pushing it into the next, the join being bound over with a slip of pasted paper. They can be made to take various angles by cutting away the paper at the elbow of the bend.

Port-fires consist of cases about 10 or 12 inches long, made very thin, usually three or four turns of paper only, and ⅜ or ¼-in. bore, filled with a slow burning mixture—such as nitre 6 parts, sulphur 2, meal powder 1.

One or two technical applications of pyrotechny other than the manufacture of fireworks for spectacular display may be briefly mentioned.

The so-called 'drain rocket' is specially made to emit large volumes of smoke, and often a powerful stench, and is used to detect leaks and stoppages in drains. In so far as it does not travel, but is stationary, the term rocket as applied to it is a misnomer. The 'trawler's flare' is a useful firework to enable fishermen to see the floats and buoys of their nets by night. It consists of a case about 4 ins. long and 1 in. diameter, filled with a flaring mixture, and attached to a wooden handle. An ingenious device is adopted to enable the men to light them in wind and rain. When the cases are loaded a small quantity of a chlorate of potash mixture is spread on the end; this is then papered over, a strip of tape being laid under the paper and its end left projecting as a little 'tab' against the side of the case. The handle is bored out, and into the hole fits a little wooden stopper or plug, the tip of which has been coated with red phosphorus. To ignite the flare the sailor pulls the tab and peels off the paper covering, and rubs the end of the wooden stopper across the mouth of the firework, when the mixture is inflamed.

A modified form of rocket is used as a means of carrying a thin line to ships in distress round the coast, forming a part of what is known as the 'rocket apparatus.' These rockets are a combination of two rockets in one case, one being a continuation of the other, so that when the discharge of the first compartment has carried the instrument to its full height the second is ignited and gives it an additional impetus, thereby greatly increasing its range.

Another valuable signal, known as the 'sound and flash rocket' (patented by Messrs. Brock), carries as its load an explosive aluminium mixture, which, as the name implies, explodes with a loud detonation and a dazzling flash of light (*see* also FLASH-LIGHTS). G. S. N.

PYROXYLIC SPIRIT (*crude Methyl alcohol*) *v.* METHYL ALCOHOL.

PYROXYLINE *v.* PHOTOGRAPHY.

PYRRHOTITE, *Pyrrhotine*, or *Magnetic pyrites*, occurs occasionally as six-sided crystals, belonging to the hexagonal system; but is usually found as granular or compact masses with a platy structure. From ordinary pyrites it is distinguished by its colour, which is bronze-yellow or tombac-brown, and by its magnetic properties, which are sometimes feeble although in rare cases the mineral exhibits polarity. It is readily scratched by the knife (hardness 3½–4½), giving a greyish streak, whence it may be distinguished from the much harder iron-pyrites. Sp.gr. 4·5–4·6. In chemical composition pyrrhotite comes very near to FeS (which requires 63·6 Fe, 36·4 S): but there is always a slight excess of sulphur, generally suggesting Fe_7S_8 (or 60·4 Fe, 39·6 S). Habermehl gives Fe_7S_8 as the formula for the variety from Bodenmais; while Lindström regards Fe_8S_9 as representing the commonest type. According to Rammelsberg, the general formula may be written Fe_nS_{n+1}, where n varies from 6–11. E. T. Allen (J. Washington Acad. Sci. 1911, 1, 170) explains the variation in composition by the solid solution of sulphur in ferrous sulphide, giving the formula $(FeS)S_x$. It is notable that nickel is very commonly present in magnetic pyrites, in some cases up to 5 or 6 p.c., and the mineral is often worked for the sake of this metal. Cobalt may also be present. The principal localities are Bodenmais in Bavaria; Falun, Sweden; Modum and Kongsberg, Norway; Sudbury, Ontario; and Morro Velho in Brazil. A similar, if not identical, material is found in most meteorites: this is known as *troilite* (FeS). F. W. R.

PYRROL-DERIVATIVES and **-DYESTUFFS** *v.* BONE OIL.

PYRROLINE *v.* BONE OIL.

PYRUVIC ACID, *pyroracemic acid*

$$CH_3{\cdot}CO{\cdot}CO_2H.$$

An acid formed by the distillation of tartaric acid and of cream of tartar; also formed by the distillation of glyceric acid or by oxidising lactic acid by means of potassium permanganate; by the photochemical decomposition of lactic acid (Ganassi, Boll. Chim. Farm. 1909, 48, 785; Zentr. Biochem. and Biophys. 1911, 11, 378); by the complete hydrolysis of protein substances such as hair (Mörner, Zeitsch. Physiol. Chem. 1904, 42, 123); by the oxidation of acetone with permanganate in alkaline solution (Fournier, Bull. Soc. Chim. 1908, [iii.] 259), or with 20 p.c. hydrogen peroxide (Pastureau, Compt. rend. 1905, 140, 1591); and by other methods (Baumann and Preuss, Zeitsch. physiol. Chem. 1881, 5, 322; Sandmeyer, Ber. 1887, 20, 641; Otto, *ibid.* 1894, 27, 838, 1264, amongst others). It has been prepared synthetically by the action of hydrochloric acid on acetyl cyanide (Claisen and Shadwell, *ibid.* 1878, 11, 1565). Thus

$$CH_3COCl+KCN=CH_3CO{\cdot}CN+KCl$$

$$CH_3CO{\cdot}CN \xrightarrow{HCl} CH_3CO{\cdot}CO_2H$$

this being a general method for the preparation of ketonic acids. It is, however, best prepared by distilling 500 grms. tartaric acid with 780 grms. commercial potassium hydrogen sulphate in a copper retort lined with asbestos and water glass. The distillate, which is collected in a well cooled receiver provided with an upright condenser, is then fractionated under reduced pressure (Wohl and Maag, *ibid.* 1910, 43, 2188; *see* also Erlenmeyer, *ibid.* 1881, 14, 320; Simon, Bull. Soc. Chim. 1895, [iii.] 13, 335).

Properties. Pyruvic acid is a liquid b.p. 59°–60°/12 mm., 165°/760 mm. solidifies at a low temperature; sp.gr. 1·2649 at 25°, 1·2881 at 4°; readily soluble in water, alcohol, or ether. It tends to polymerise on standing (Wolff, Annalen, 1899, 305, 156. It combines with nascent hydrogen to form lactic acid (Rockwell, J. Amer. Chem. Soc. 1902, 24, 719; Tafel and Friedrichs, Ber. 1904, 37, 3187).

Pyruvic acid has all the properties of a ketone, yielding an oxime, hydrazone (m.p. 192°), addition product with hydrogen cyanide, &c.

When heated alone to 170°, or with acids to

100°–150°, carbon dioxide is evolved, and a variety of products are formed (Hanriot, Bull. Soc. chim. 1885, 43, 417; *ibid.* 1886, 45, 81; Perdrix, *ibid.* 1900 [iii.] 23, 645; De Jong, Rec. trav. chim. 1901, 20, 81; *ibid.* 1902, 21, 191; *ibid.* 1903, 22, 281; *ibid.* 1904, 23, 147). With hydrogen peroxide it forms acetic acid and carbon dioxide (Holleman, *ibid.* 1904, 23, 169). When boiled with concentrated sodium hydroxide it yields oxalic acid.

Pyruvic acid combines with hydrocarbons (Böttinger, Ber. 1881, 14, 1595); with urea and urethane (Simon, Compt. rend. 1901, 133, 535, 587; *ibid.* 1903, 136, 506; *ibid.* 1906, 142, 790); with benzaldehyde (Erlenmeyer, Ber. 1901, 34, 817); phenols (Böttinger, *ibid.* 1883, 16, 2071); with hippuric acid (Erlenmeyer and Arbenz, Annalen, 1904, 337, 302), and with other substances.

Tests.—In addition to the ordinary ketonic tests, 1 c.c. of the acid may be added to an equal bulk of ammonia solution, when a few drops of sodium nitroprusside are added a violet-blue colour is formed, which becomes more and more greenish as the solution is diluted; when heated the colour fades slowly to an orange-red, and on boiling it disappears altogether. The only other substance which gives this reaction is acetophenone, which can be distinguished from it by Legal's reaction (Simon, Compt. rend. 1897, 125, 534). When 1 drop of pyruvic acid is added to 10 drops of a freshly prepared solution of α- or β-naphthol (0·02 grm. to 0·05 grm.) in sulphuric acid (1 c.c.) of sp.gr. 1·83, and the mixture is warmed gently, a bright red colour is obtained with β-naphthol in the cold, and an intense blue on warming; if water or alcohol is added, a fugitive yellow colour is produced. With α-naphthol the colour is yellow in the cold, intense orange on warming and the colour remains on addition of water or alcohol (Alvarez, Bull. Soc. chim. 1905, 33, 716). All fatty amines when added to a mixture of pyruvic acid and sodium nitroprusside produce a deep violet colour, which, on addition of acetic acid, turns blue, and disappears rapidly (Simon, *l.c.*)

Pyruvic acid forms a number of unstable salts, which pass into gummy masses on heating, but are crystalline in the cold (Wolff, *l.c.* De Jong, *l.c.* 1901, 20, 365). It also forms esters, amide, nitrile, imino, sulpho and halogen derivatives.

For the physiological properties of pyruvic acid, *see* Pohl (Arch. Exp. Path. Pharm. 1896, 37, 422), Mörner (Zeitsch. physiol. Chem. 1904, 42, 121), Embden and Schmitz (Biochem. Zeitsch. 1910, 29, 423).

The free acid, but not the sodium salt, acts as a strong poison to wheat seeds (Schreiner and Shorey, J. Amer. Chem. Soc. 1908, 30, 1306).

Q

QUARTATION *v.* Assaying.

QUARTZ. The most abundant of minerals composing the earth's crust, and one which appears in a greater variety of forms and modes of occurrence than any other mineral. It is anhydrous silica (SiO_2) crystallised in the rhombohedral system, the degree of symmetry being that of the trigonal-trapezohedral class. The crystals, which are often beautifully developed, are usually bounded by a hexagonal prism and terminated by a six-sided pyramid, the latter being in reality a combination of two rhombohedra. The angle between the normals to the prism and pyramid faces is 38° 13′ (*i.e.* the angle of slope of the pyramid is 51° 47′); and the rhombohedral angle is 85° 46′, so that when only one rhombohedron is developed the crystals have the appearance of cubes. Specially characteristic features, always of assistance in the identification of the mineral, are the presence of horizontal striations on the prism faces and the absence of a basal plane perpendicular to the prism. With the development of certain, comparatively rare, trapezoidal faces on the corners between the prism and the pyramid, the crystals betray a helical nature which is inherent in their structure. As shown by the disposition of these extra faces, some crystals are right-handed and others are left-handed; the two kinds, although similar and mirror-reflections the one of the other, are non-superposable—such crystals are said to be enantiomorphous (a similar relation is also shown by crystals of tartaric acid).

The helical structure of quartz is also impressed on the optical properties of the crystals, which are circularly polarising in the direction of the principal axis. When a beam of plane-polarised light traverses a quartz crystal in a direction parallel to the vertical edges of the prism, the plane of polarisation is rotated to the right or to the left, according to whether the crystal is a right-handed or a left-handed one. On this property depends the use of quartz plates, cut perpendicular to the prism edges, in polarimeters and saccharimeters. A plate of quartz 1 mm. in thickness rotates the plane of polarisation of sodium (D) light through 22° and of blue (G) light through 43°. The mineral is optically uniaxial with positive double refraction (refractive indices are quoted below in a footnote).

Crystals of quartz possess no distinct cleavage; they break with a bright and glassy conchoidal fracture, and small fragments have sharp splintery edges. Fractured surfaces sometimes exhibit a minute rippled marking, like the marks made when the thumb is pressed against a plastic surface; this is especially characteristic of the amethyst variety, and is due to the lamellar intergrowth of right-handed and left-handed quartz. (Sections of such intergrowths exhibit 'Airy's spirals' in the polariscope.) The mineral readily scratches glass, and itself cannot be scratched by steel; it is selected as No. 7 in the mineralogist's scale of hardness. These characters are of much help for the recognition of the mineral when crystal-faces are not developed. The sp.gr. is 2·65.

Quartz is very resistant to chemical reagents and to weathering processes. For this reason, when rocks are weathered and disintegrated the quartz remains as the ubiquitous quartz-sand. It is insoluble in acids, with the exception of hydrofluoric, and is only slightly attacked by solutions of caustic alkalis (in which hydrated silica and opal are soluble). When fused with sodium carbonate, it yields sodium silicate; it is slowly attacked by fused borax, but not by microcosmic salt. It is slightly soluble in superheated water and in superheated solutions of sodium silicate and sodium borate (*see* G. Spezia, Atti Accad. Sci. Torino, 1895 *et seq.*, on the solubility of quartz and the artificial growth of quartz crystals).

When quartz is heated it undergoes a series of remarkable changes. In the first place, it usually decrepitates violently, owing to the presence of vast numbers of microscopic cavities containing water and liquid carbon dioxide (W. N. Hartley, Chem. Soc. Trans. 1876, i. 137; 1877, i. 241). At 575° (or 570°) there is an abrupt change in the coefficients of thermal expansion, the circular polarisation, and the refractive indices.[1] This change from α-quartz to β-quartz (stable above 575°) is a reversible or enantiotropic one. From etching experiments on basal sections, O. Mügge (Jahrb. Min. 1907, Festband, 181) has shown that the two forms differ in their crystalline symmetry, α-quartz being trigonal-trapezohedral and β-quartz hexagonal-trapezohedral. This has an important bearing on geological problems; and, as shown by F. E. Wright and E. S. Larsen (Quartz as a Geologic Thermometer, Amer. J. Sci. 1909, 27, 421), it is possible to determine whether in any particular instance the mineral has been formed at a temperature above or below 575°. At a still higher temperature (about 800°) the β-quartz is transformed into tridymite (an orthorhombic modification of silica with sp.gr. 2·32). This enantiotropic change takes place but slowly, and is accompanied by a considerable alteration in volume. At about 1600° the material (now tridymite, or perhaps cristobalite) begins to melt to an extremely viscous liquid, so that the exact melting-point cannot be determined. The molten material, if not cooled too slowly, consolidates as a glass with sp.gr. 2·213 (A. L. Day and E. S. Shepherd, Amer. J. Sci. 1906, 22, 273; C. Johns, Geol. Mag. 1906, 3, 118).

This vitrified silica or silica-glass (also called quartz-glass; but the terms 'quartz fibres,' 'quartz tubes,' and 'quartz vessels' are scarcely correct, since the material is no longer quartz) possesses certain remarkable properties. It has an extremely low coefficient of thermal expansion, and can consequently be subjected to sudden changes of temperature without cracking; it is highly transparent for ultra-violet rays, and is a non-conductor of electricity even in a moist atmosphere and at high temperatures; it possesses a high degree of elasticity, and is unaffected by many chemical reagents. The material therefore finds many useful applications in chemical and physical apparatus (W. A. Shenstone, Proc. Roy. Inst. 1902, 16, 525; Nature, 1901, 64, 65).

The characters so far considered are the essential characters of the mineral; in its unessential characters it exhibits a remarkably wide range of variation, so much so that at times the essential characters, useful for purposes of determination, may become masked. In size the crystals may range from mere shining specks (producing a drusy effect on rock surfaces) to those measuring a yard in length and diameter and weighing half a ton. The material may be perfectly transparent or quite opaque, splendent or dull, and of almost any shade of colour. Further, in the massive material there may be different modes of aggregation of the crystalline particles; and impurities of various kinds may be intermixed with the quartz substance. For these reasons a large number of varieties of quartz, differing widely in their external appearance, have been from the earliest times distinguished by special names; and it was only with the rise of chemical science that their true nature was determined.

The following more important *varieties* may be mentioned:—

A. Crystallised quartz with vitreous lustre:
  Rock-crystal or 'crystal' (the κρύσταλλος of the ancients), the purest form of quartz, the crystals being colourless and water-clear ('Marmorosch diamonds,' 'Bristol diamonds,' 'Brazilian pebble,' &c.).
  Amethyst (*q.v.*), of a violet colour.
  Cirtine, yellow varieties; the 'occidental topaz,' 'Spanish topaz,' &c., of jewellers.
  Smoky-quartz and *Cairngorm* (*q.v.*), of a smoke-grey, brownish, or black colour.
  Rose-quartz, of a delicate rose-red (never found as crystals bounded by faces).
  Milk-quartz, white, with milky opalescence.
  Sapphire-quartz, of a blue colour.
  Prase, leek-green colour.
B. Quartz with enclosures:
  Avanturine-quartz, enclosing scales of mica, hæmatite, &c.
  Cat's-eye and *Tiger-eye* (*v.* CROCIDOLITE) enclosing fibres of asbestos.
  Hair-stone, *Needle-stone*, &c., enclosing needles of rutile, actinolite, &c.
  Eisenkiesel, enclosing iron oxide and hydroxides.
C. Cryptocrystalline quartz (Chalcedony), with waxy lustre:
  Agate (*q.v.*), with curved bands differently coloured.
  Onyx, with straight bands differently coloured.
  Carnelian (or *cornelian*), yellowish-red or orange.
  Sard, yellowish-brown.
  Chrysoprase, pale green.
  Plasma, dark green.
  Bloodstone (*q.v.*) or *Heliotrope*, dark green with red spots.
D. Compact varieties, with dull lustre:
  Jasper (*q.v.*).
  Flint (*q.v.*).
  Lydian stone (*q.v.*).
  Buhrstone (*q.v.*).

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[1] F. Rinne and R. Kolb (Jahrb. Min. 1910, ii. 138) have made a large number of determinations of the refractive indices of quartz at temperatures ranging from −140° to +765°; *e.g.* at 23° (α-quartz) for the line D_2, $\omega = 1{\cdot}5442$, $\epsilon = 1{\cdot}5533$, $\epsilon - \omega = 0{\cdot}0091$, and at 580° ($\beta$-quartz), $\omega = 1{\cdot}5328$, $\epsilon = 1{\cdot}5404$, $\epsilon - \omega = 0{\cdot}0076$. Determinations of the birefringence and rotatory power over a wide range of temperature have been made by F. E. Wright and E. S. Larsen (Amer. J. Sci., 1909, 27, 421).

Other varieties, partaking more of the nature of rocks, are sand (*q.v.*), sandstone (*q.v.*), quartzite, vein-quartz, oilstone (*q.v.*), whetstone (*q.v.*), &c.

In its *modes of occurrence* quartz is equally varied. It is an important essential constituent of many of the primary rocks (gneiss, schist, granite, &c.), and with the breaking down of these it enters largely into the composition of the secondary sedimentary rocks (sandstone, &c.). It is a common product of decomposition of silicate minerals, and it is consequently abundant in veins and cavities in altered rocks and as pseudomorphs after numerous other minerals. In mineral-veins it is the commonest of the gangue materials. The several varieties each have, to a certain extent, their own modes of occurrence. For example, rock-crystal is found in veins traversing gneissic rocks and in pegmatite; amethyst is more frequently found in the geodes of weathered basic rocks (melaphyre), although also in granite and in mineral-veins.

The *uses* of quartz are also numerous. Many of the coloured varieties are employed in jewellery as semi-precious stones, for engraving, and for small ornaments of various kinds; and also, to a certain extent, as an ornamental stone in buildings. Balance weights, pivot supports, agate mortars, &c., are also cut in quartz. The 'Brazilian pebble' of the spectacle maker is clear rock-crystal from Brazil and Madagascar; and the same material is also cut into prisms, plates, and wedges for optical apparatus. As an abrasive agent quartz finds an extensive application in the form of grindstones, millstones, oilstones, whetstones, sand-paper, scouring soap, polishing materials, sand blasts, &c. For the latter purpose ground quartz is more efficacious than quartz-sand, since the particles are more angular and sharper. Ground quartz is also used as a wood-filler, in the manufacture of paints (to which it imparts 'tooth') and in filters. The massive white quartz used for grinding is quarried from veins or obtained as a by-product in felspar mining, mainly in the United States, Ontario, and Sweden. The blocks are heated in kilns and fractured by spraying with water, crushed, and then ground in edge-runners or between rollers, either in a dry or wet condition. Quartz and quartz-sand are also largely used in building; in making cements and mortar; in the manufacture of glass and silica-glass, pottery and pottery glazes, ferrosilicon, and carborundum. It is also used to a certain extent as a flux in copper smelting. Blocks of quartz or quartzite are sometimes used for filling acid towers.

References.—For a detailed *résumé* of the literature on the mineralogical characters and occurrence of quartz, *see* C. Hintze, Handbuch der Mineralogie, 1904–6, i. 1266–1445. On its uses as a gem-stone, M. Bauer, Precious Stones, English translation, 1904, by L. J. Spencer. On economic uses, G. P. Merrill, The Non-metallic Minerals, 2nd ed. 1910; and Mineral Resources, United States Geological Survey.

L. J. S.

QUASSIA. *Bitter-wood* (*Bois de Quassia*, Fr.; *Quassiaholz*, Ger.). The wood of *Picræna excelsa* (Lindley), a large ash-like tree inhabiting the plains and lower mountain slopes of Jamaica and neighbouring islands (*v.* Bentl. a. Trim. 57). Formerly the quassia of commerce was derived from the allied South American tree *Quassia amara* (Linn.), and the wood of this tree is still employed on the continent. *Picrasma quassioides* (Benn.) and *Samadera indica* (Gaertn.) also furnish a very similar wood (Pharm. J. [iii.] 2, 644, 654; 20, 41). The intensely bitter taste of the wood of *P. excelsa* is due to the presence of about 0·03 p.c. of a neutral crystalline substance, *quassin.* Compounds possessing similar properties have been isolated from the other trees mentioned; indeed, it was from *Q. amara* that quassin was first isolated by Winckler (Rep. Pharm. 54, 85; 65, 74). It was analysed and further studied by Wiggers, who obtained it from an aqueous infusion of the wood, after separation of pectinous constituents by means of lime or lead carbonate, by evaporation to dryness and extraction with alcohol. The alcoholic solution yielded a crude quassin, which, after purification, assumed the form of white opaque prisms. Dissolved in water, quassin thus obtained gives no precipitate with chlorine, iodine, mercuric chloride, or salts of lead or iron, but forms an insoluble compound with tannin (Annalen, 21, 40).

Improved methods for the preparation of quassin were proposed by Christensen (Arch. Pharm. [iii.] 20, 481), and by Adrian and Moreaux (Rép. de Pharm. 11, 246). Christensen prepares an insoluble tannate directly from a neutralised aqueous infusion of the wood, and this, decomposed by lime or lead carbonate, yields a crude quassin to alcohol. Adrian and Moreaux take advantage of the easy solubility of quassin in alkalis, and extract the wood with water containing alkaline carbonate. The infusion is evaporated and treated with alcohol, when a solution is obtained which, after several processes of purification, yields quassin in crystals.

According to Oliveri and Denaro (Gazz. chim. ital. 14, 1; 15, 6), who employ for its preparation a modified form of Christensen's method, quassin consists of slender colourless iridescent needles, which melt at 210°–211°. It has the formula $C_{32}H_{42}O_{10}$. It is very soluble in alcohol, chloroform, or acetic acid, but nearly insoluble in ether. 100 parts of water at 22° dissolve 0·253 parts of quassin. Heated with hydrochloric acid in a sealed tube, it yields two molecules of methyl chloride and *quassic acid*

$$C_{30}H_{33}O_{10},H_2O$$

a compound melting at 245° and crystallising in silky needles. Oliveri and Denaro are thus led to regard quassin as a dimethyl ether of quassic acid, $C_{28}H_{36}O_6(COOCH_3)_2$. The composition of the metallic salts of quassic acid also shows that it is dibasic. Oliveri (Gazz. chim. ital. 17, 570), by acting on the acid with hydroxylamine hydrochloride obtains a *dioxime* $C_{28}H_{38}O_8(C{:}NOH)_2$, in yellow prisms which melt at 228°–230°. The existence of this compound indicates that quassic acid contains two ketonic CO groups. That this is also the case with its dimethyl derivative quassin, is further shown by Oliveri (Gazz. chim. ital. 18, 169) by the formation of a *phenylhydrazine compound*, $C_{30}H_{42}O_8(CN{\cdot}NHC_6H_5)_2$, by the action of that reagent on quassin.

Quassin reduces Fehling's solution, but when it is heated with dilute sulphuric acid no sugar is formed. By this treatment it loses a molecule of water, forming an anhydride, *quasside*, $C_{32}H_{40}O_9$. This compound, which is white, amorphous, and bitter, melts at 192°–194° and when boiled with dilute alcohol, takes up again a molecule of water, quassin being re-formed. Quassin may also be converted into the anhydride by heating with acetic anhydride, or even by heat alone at 150° in a current of dry air. If bromine be present *tribromoquasside*, $C_{32}H_{37}Br_3O_9$, results. If quassin be heated with acetic anhydride in presence of sodium acetate the dehydration goes further. In this case two molecules of water are removed, and a *second anhydride*, $C_{32}H_{38}O_8$, a white, pearl-like, amorphous mass, melting at 150°–158°, is obtained. Bromine forms with quassin a substitution derivative melting at 155°, *bromoquassin*, $C_{32}H_{41}Br_3O_9$ (?), and phosphorus pentachloride yields *pentachloroquassin*, $C_{32}H_{39}Cl_5O_9$ (?), a yellow powder melting at 119°. A *nitro derivative* melting at 130° also exists (D. and O.). When quassin is heated with concentrated hydriodic acid and amorphous phosphorus it yields, among other products, *isodurene*, $C_{10}H_{14}$, and a *hydrocarbon*, $C_{14}H_{16}$, which boils at 220°–240° (Oliveri, Gazz. chim. ital. 17, 575).

From the investigations of Massute (Arch. Pharm. [iii.] 28, 147) it would appear that the bitter crystalline constituents of the different trees mentioned at the beginning of this article, although similar, are not identical. By an improved process this observer obtains from the wood of *Q. amara* four bitter crystalline *quassins*, one of which corresponds with the quassin of Oliveri and Denaro. The others are probably methyl derivatives of this with higher melting-points. From *P. excelsa* the same chemist obtains two crystalline compounds which are designated *picrasmins*. They differ in composition from the *quassins*, but appear also to be methyl derivatives or homologues. One of them yields, by the action of hydrochloric acid, *picrasmic acid*, homologous with the quassic acid of Oliveri and Denaro. By extracting crude quassin with ether, Merck (Chem. Zentr. 1895, i. 435) obtained *quassole* $C_{46}H_{70}O+H_2O$ (?) which crystallises in colourless plates melting at 149°–151°. It differs from quassin by its absence of taste.

Quassia is sometimes used as a substitute for hops in beer. For methods of its detection see Dragendorff (Chem. Zentr. 1881, 285 and 299), Allen (Analyst. 1887, 107), Chapman (*ibid.* 1900, 35). A. S.

QUASSIC ACID, QUASSIDE, QUASSIN, *v.* Quassia.

QUEBRACHO COLORADO. The quebracho colorado are anacardiaceous trees belonging to the genus *Quebrachia*, growing in the northern part of the Argentine Republic, the wood of which constitutes the well-known tannin substance 'quebracho.' It is imported into this country in the form of logs and is employed for tanning, either in the chipped condition or in the form of extract. Their wood is extremely hard, as the name 'quebracho' (axe-breaker) denotes, and its sp.gr. varies from 1·27 to 1·38.

Jean (Bull. Soc. chim. 1880, 33, 6) found that it contained 15·7 p.c. of a tannic acid not identical with that of oak bark or chestnut wood, whereas Procter (Leather Manufacture, 1903, 269) estimates it to contain about 20 p.c. of a tannin yielding reds (phlobophane) and containing catechol and phloroglucinol nuclei. This tannin is somewhat sparingly soluble in water and can only be used in weak liquors, but gives a firm reddish leather.

In order to isolate the tannin, Strauss and Geschwender (Zeitsch. angew. Chem. 1906, 19, 1121) extract the bark first with chloroform and then with alcohol. Addition of water to the alcoholic extract causes the separation of phlobophanes, and from the clear liquid concentrated in a vacuum the tannin is precipitated by lead acetate, the lead salt being collected suspended in water and decomposed with sulphuretted hydrogen. The resulting solution is evaporated to dryness, the residue dissolved in alcohol and poured into ether. Thus obtained it consists of a light flaky mass, which is hygroscopic and becomes sticky on exposure to moist air.

According to Arata (J. 1879, 306), *quebracho tannin* $C_{26}H_{24}O_{10}$ gives *catechol* on dry distillation, with nitric acid *oxalic* and *picric acids*, by fusion with alkali *phloroglucinol* and *protocatechuic acid*, whereas, by the latter method, Nierenstein isolated also *hydroquinone* and *resorcinol* (Collegium, 1905, 65). According to the latter author, the quebracho colorado probably contains three tannins. By treating a cold aqueous extract of the quebracho colorado with bromine, Böttinger (Ber. 17, 1123) obtained a reddish-yellow compound containing 42·1 to 44·5 p.c. of bromine. Neirenstein, who isolated the tannin according to Trimble's method (The Tannins), treated the solution with lead acetate, filtered, and on adding bromine to the clear liquid obtained a precipitate of *monobromoquebrachotannin* $C_{16}H_{14}Br{\cdot}O_8$, which consists of a cinnabar red powder, and on digestion with alcoholic potash gives iso*vanillic acid* and *monobromoquebrachylic acid* needles, m.p. 119°–120°.

Strauss and Geschwender (*l.c.*) consider that quebracho tannin is identical with malettotannin, and with the tannin from cinchona bark, and ascribe to it the formula $C_{43}H_{50}O_{20}$. With a mixture of acetic anhydride and acetic acid the *acetyl* compound $(C_{30}H_{22}O_{11}Ac_6)_2$, colourless powder, is produced, and a corresponding *benzoyl* derivative $(C_{30}H_{22}O_{11}Bz_6)_2$ can also be prepared.

Quebracho phlobophane, on distillation with zinc dust, yields anthracene (Nierenstein, Ber. 1907, 40, 4575).

According to Arnaudon the wood contains a colouring matter which gives a fine yellow dye, and this has been examined by Perkin and Gunnell (Chem. Soc. Trans. 1896, 69, 1304) and found to be identical with *fisetin*, the colouring matter of young fustic. This compound, which appears to exist in the wood as glucoside, gives on fusion with alkali protocatechuic acid and resorcinol, and may account for the appearance of the latter phenol among the hydrolytic products of the crude tannin itself. According to Perkin and Gunnell, when an extract of the quebracho colorado is digested with boiling dilute acid a small quantity of *ellagic acid* is obtained.

In addition to the tannins above described, the quebracho colorado is the source of the so-called 'quebracho resin,' which collects as a thickened juice in the crevices of the tree. It has been examined by Arata (Chem. Soc. Abstr.

1878, 984) who describes it as easily soluble in alcohol or ethyl acetate, insoluble in benzene. By fusion with alkali it gives *protocatechuic acid* (?) and *phloroglucin*, and by the action of nitric acid, oxalic and picric acids are produced.

A considerable amount of the tannin contained by the quebracho colorado is of a sparingly soluble nature, and is deposited to some extent from a hot aqueous extract on cooling. This product may be rendered soluble by treatment with alkalis or alkaline sulphites and a large quantity of the so-called 'soluble' quebracho extracts are prepared by heating the material in closed vessels with bisulphites, sulphites, sulphides or even caustic alkalis (Lepetit, Dollfus and Gansser, Eng. Pat. 1896, 8582; *cf.* Procter, Leather Manufacture, 338). A. G. P.

QUEBRACO or **QUEBRACHO BARK**, the bark of *Aspidosperma Quebracho* (Schlecht.), obtained from the Argentine Republic, is used for medicinal purposes (*v.* VEGETO-ALKALOIDS).

QUERCETAGETIN. Quercetagetin, the yellow colouring matter of the flowers of *Tagetes patula* (Linn.) (African marigold), was first isolated by Latour and Magnier (Bull. Soc. Chim. [ii.] 28, 337), who assigned to it the formula $C_{27}H_{22}O_{13},4H_2O$. It has been examined since by Perkin (Chem. Soc. Proc. 1902, 18, 75), who suggests the formula $C_{15}H_{10}O_8$. Quercetagetin crystallises in pale yellow needles, dissolves in alkaline solutions with a yellow colour, and dyes mordanted fabrics somewhat similarly to quercetin. *Acetyl quercetagetin*, $C_{15}H_4O_8(C_2H_3O)_6$, colourless needles, m.p. 209°–211°, *quercetagetin sulphate* $C_{15}H_{10}O_8{\cdot}H_2SO_4$, orange-red needles, and *Monopotassium quercetagetin*, $C_{15}H_9O_8K$, have been prepared. On fusion with alkali quercetagetin gives *protocatechuic acid* and is in reality a hexahydroxyflavone isomeric with myricetin.

A. G. P.

QUERCETIN *v.* HORSE CHESNUT and QUERCITRON BARK.

QUERCIMETRIN *v.* GLUCOSIDES.

QUERCIN; QUERCEMIC ACID *v.* TANNINS.

QUERCITE *v.* INOSITE.

QUERCITRIN *v.* GLUCOSIDES.

QUERCITRON BARK. This important yellow dyestuff, the latest addition to the somewhat meagre list of commercial natural colouring matters, was discovered and introduced by Bancroft in 1775. In his Philosophy of Permanent Colours he states (II, 113), 'Quercitron bark is one of the objects of a discovery of which the use and application for dyeing are exclusively vested in me, for a term of years by an Act of Parliament in the twenty-fifth year of his present Majesty's reign.'

Quercitron bark is the inner bark of a species of oak known as *Quercus discolor* (Ait.) [*Q. tinctoria*], which is a native of the Middle and Southern States of America. The tree in the south is described as being from 60 to 80 ft. high, with a trunk from 6 to 10 ft. in diameter; but in the north it does not attain to this size. In order to obtain the dyestuff the epidermis or exterior blackish coat of bark is usually removed by shaving and the inner portion then detached and ground. The product may be separated into stringy fibres and a light fine powder, the latter of which contains the principal portion of the colouring matter.

Quercitron bark and its preparations are still used to a considerable extent, although not so much as was formerly the case. This is not only due to the introduction of the artificial colouring matters, but because it has been supplanted for many purposes by the less costly Old Fustic.

Quercetin $C_{15}H_{10}O_7$, the colouring matter of quercitron bark, has been the subject of numerous researches, and many of these unfortunately resulted in the publication of complicated and unsatisfactory formulæ. At an early stage it was ascertained that quercetin does not exist in the plant, at least to any extent in the free condition, but in the form of its glucoside *quercitrin.*

To prepare quercetin the following method devised by the late Sir W. H. Perkin, and employed by him for several years on the manufacturing scale, gives good results. Quercitron bark dust is macerated with moderately strong salt solution to remove gummy substances, filtered, and then extracted with dilute ammonia. The cold ammoniacal liquid is treated with a slight excess of hydrochloric acid, causing the separation of certain impurities in the form of a brown flocculent precipitate. This is removed, and the pale yellow acid solution of the glucoside is boiled for about 30 minutes. The glucoside is thus hydrolysed and almost chemically pure quercetin separates in the form of pale yellow needles, which are collected while the mixture is still warm and washed with water. It is readily soluble in alcohol, and dissolves in alkaline solutions with a yellow colour. With aqueous lead acetate it gives a bright orange-red precipitate, and with alcoholic ferric chloride a dark green colour.

The most important of the early investigations of quercetin was carried out by Liebermann and Hamburger (Ber. 12, 1178), who assigned to it the formula $C_{24}H_{16}O_{11}$, and to quercitrin the formula $C_{36}H_{38}O_{20}$. Herzig (Monatsh. 5, 72; 6, 863; 9, 537; 12, 172; 14, 53; 15, 697), who has carried out an elaborate series of researches on this subject, at first adopted this formula. Subsequently it was ascertained that quercetin was in reality $C_{15}H_{10}O_7$, and this received support by the preparation of its compounds with mineral acids by Perkin and Pate (Chem. Soc. Trans., 1895, 67, 647).

When quercetin is fused with alkali, it gives *protocatechuic acid* and *phloroglucinol*, and if its alkaline solution is oxidised with air, the same products are obtained. By the more gentle action of the alkali Hlasiwetz and Pfaundler (J. 1864, 561) obtained certain intermediate products of the hydrolysis, *paradiscetin* $C_{15}H_{10}O_6$, yellow needles, *quercetic acid* $C_{15}H_{10}O_7$, colourless needles, and *quercimeric acid* $C_8H_6O_5,H_2O$, colourless crystals. Herzig and others who have reinvestigated this decomposition have been unable to obtain the substances of Hlasiwetz and Pfaundler, and if these compounds are in reality chemical individuals, it seems likely that their formation was due to the action of some special impurity contained in the alkali employed by these chemists.

On acetylation quercetin gives a *pentaacetyl compound* $C_{15}H_5O_7(C_2H_3O)_5$, colourless needles, melting at 191°–195°, but on methylation with methyl iodide the *tetramethyl ether* $C_{15}H_6O_3(OCH_3)_4$, long yellow needles, m.p. 156°–157° (H.) is produced. A free hydroxyl group is still present in this compound, and it yields with alcoholic potash a bright yellow salt decomposable by water, and a *monoacetyl* derivative $C_{15}H_5O_3(C_2H_3O)(OCH_3)_4$, needles, m.p. 167°–169° (H.). The *ethylation* product

$$C_{15}H_6O_3(OC_2H_5)_4$$

yellow needles, m.p. 120°–122°, is similarly constituted, and gives the *acetyl* compound $C_{15}H_5O_3(OC_2H_5)_4(C_2H_3O)$, m.p. 151°–153°.

When heated with alcoholic potash, quercetin tetramethyl ether forms *veratric acid* and a syrupy phloroglucinol derivative (H.), and this latter has been shown (Perkin and Allison, Chem. Soc. Trans. 1902, 81, 471) by means of its disazobenzene derivative to consist of *phloroglucinol monomethyl ether.* Quercetin tetraethyl ether exhibits a similar behaviour.

The following is a list of the more important derivatives of quercetin: *Dibromquercetin* $C_{15}H_8Br_2O_7$, yellow needles, m.p. 233°–235° (H.), *acetyl dibromquercetin* $C_{15}H_3Br_2O_7(C_2H_3O)_5$ (H.), *dibromquercetin tetraethyl ether*, yellow needles, m.p. 169°–173°, *quercetin triphenylcarbamide* $(OH)_2\cdot C_{15}H_5O_5(OCO\cdot NH\cdot C_6H_5)_3$ (Tesmer, Ber. 1885, 18, 2609), *triacetyl quercetin*

$$C_{15}H_7O_7(C_2H_3O)_3,$$

colourless needles, m.p. 167°–169°, and *tetraacetyl quercetin* $C_{15}H_6O_7(C_2H_3O)_4$, m.p. 193°–194° (Perkin, Chem. Soc. Trans. 1899, 75, 449), *benzoyl quercetin* $C_{15}H_5O_7\cdot(C_7H_5O)_5$, m.p. 239° (Dunstan and Henry, Chem. Soc. Trans. 1898, 73, 219). With mineral acids in the presence of acetic acid, quercetin gives *quercetin sulphate* $C_{15}H_{10}O_7\cdot H_2SO_4$, *quercetin hydrobromide*

$$C_{15}H_{10}O_7\cdot HBr$$

quercetin hydrochloride $C_{15}H_{10}O_7\cdot HCl$, and *quercetin hydriodide* $C_{15}H_{10}O_7\cdot HI$, which crystallise in orange needles and are decomposed by cold water (P. and P.). *Monopotassium quercetin* $C_{15}H_9O_7K$ and *monosodium quercetin* $C_{15}H_9O_7Na$, orange needles, are produced by the action of alcoholic potassium and sodium acetates (Perkin, Chem. Soc. Trans. 1899. 75, 438). *Aminoquercetin* $C_{15}H_4O_2(OH)_5NH_2$, pale yellow needles, has been obtained by Watson (Proc. Chem. Soc. 1911, 27, 163) by the action of hydriodic acid (1·7) on aminopentamethylquercetin. The *hydrochloride* $C_{15}H_{11}O_7\cdot N\cdot HCl$, yellow needles, the *hydriodide, sulphate*, and *acetyl* derivative, colourless rhombs, m.p. 151°–153°, are also described. Aminoquercetin dyes mordanted wool browner and deeper colours than quercetin itself.

Quercetin is a strong dyestuff, and gives with mordanted wool the following shades, which are almost indentical with those produced by fisetin:—

Chromium	*Aluminium*	*Tin*	*Iron*
Red-brown	Brown-orange	Bright orange	Olive-black

The suggestion that quercetin was probably *hydroxyfisetin* is due in the first place to Herzig, and this has been substantiated by the synthesis of this colouring matter (*see* below).

It has been found (Waliaschko, Arch. Pharm. 1904, 242, 225) that by employing methyl sulphate in the methylation of quercetin, *quercetin pentamethyl ether* $C_{15}H_5O_2(OCH_3)_5$, colourless needles, m.p. 148°, can be produced.

From quercetin pentamethyl ether Watson (Proc. Chem. Soc. 1911, 27, 163) has prepared the following compounds: *Nitropentamethylquercetin* $C_{15}H_4O_2(OCH_3)_5\cdot NO_2$, yellow needles, m.p. 202°–204°, *aminopentamethylquercetin* $C_{15}H_4O_2(OCH_3)_5\cdot NH_2$, colourless prisms, m.p. 200°–202°, *pentamethylquercetin hydrobromide* $C_{20}H_{20}O_7\cdot HBr$, *hydrochloride* $C_{20}H_{20}O_7\cdot HCl$, *sulphate* $C_{20}H_{20}O_7\cdot H_2SO_4$, *nitrate*

$$C_{20}H_{20}O_7\cdot HNO_3,$$

yellow needles, *trinitropentamethylquercetin* $C_{15}H_2O_2(OCH_3)_5(NO_2)_3$, m.p. 190°–205°, *dibrompentamethylquercetin* $C_{15}H_3O_2\cdot Br_2\cdot(OCH_3)_5$, colourless prisms, m.p. 173°–175°, *dibrompentamethylquercetin hydrobromide* $C_{20}H_{18}O_7\cdot Br_2\cdot HBr$, *dibromnitropentamethylquercetin*

$$C_{15}H_2O_2Br_2\cdot(OCH_3)_5NO_2,$$

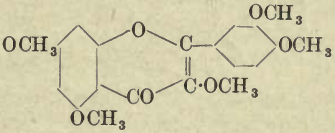
yellow rhombs, m.p. 173°–175°, *pentamethylquercetin diazonium chloride*

$$C_{15}H_4O_2\cdot(OCH_3)_5\cdot N_2\cdot Cl,$$

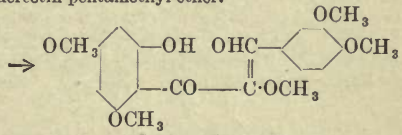
yellow needles, *sulphate* yellow needles, and *pentamethylquercetin-azo-β-napthol*

$$C_{15}H_4O_2(OCH_3)_5\cdot N_2\cdot C_{10}H_6OH.$$

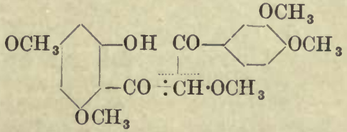
Pentamethylquercetin, when hydrolysed with alcoholic potash (Herzig, Ber. 1909, 42, 155), gives, together with *veratric acid*, the *methoxy derivative of the fisetol dimethyl ether*, which he obtained (Monatsh. 1891, 12, 187) by the hydrolysis of fisetin tetramethyl ether. The reaction may be expressed as follows:—



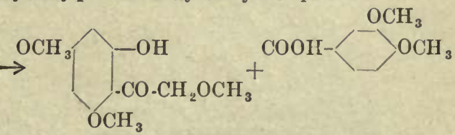
Quercetin pentamethyl ether.



Intermediate compound.

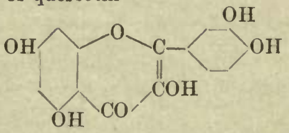


Hydroxy pentamethoxybenzoylacetophenone.



Methoxy fisetol dimethyl ether.

and affords a clear proof of the flavonol constitution of quercetin—



Quercetin has been synthesised by v. Kostanecki, Lampe, and Tambor (Ber. 1904, 37, 1402) by a series of reactions similar to those which had been successfully employed for the preparation of fisetin. The starting-point of the synthesis was 2′ hydroxy, 4′, 6′, 3, 4, tetramethoxychalkone, and the following formulæ indicate the procedure adopted (compare fisetin):—

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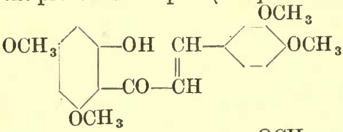

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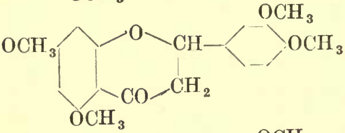

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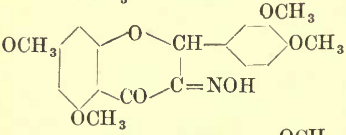

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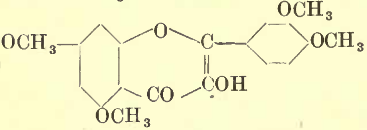

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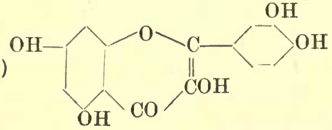
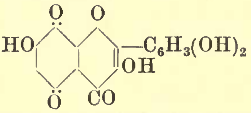
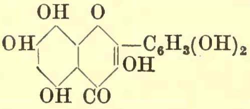


According to Nierenstein and Wheldale (Ber. 1911, 44, 3487) quercetin by oxidation with chromic acid is converted into *quercetone*, deep red needles (m.p. above 300°) which, like anthrocyanin, dissolves in alkali hydroxides with a blue and in sulphuric acid with a red colouration. It possesses the formula



(compare Kostanecki and Tambor, Ber. 1902, 35, 1869; *ibid.* 1906, 39, 4012). When heated with zinc dust and acetic anhydride yields the acetyl derivative (amorphous) of the hydroxyquercetin



This pentahydroxyflavonol, yellow needles, melts at 352–355°, gives a colourless *hexamethyl derivative* m.p. 147–149°.

Quercitrin, the glucoside of quercetin, was first isolated from quercitron bark by Chevreul, and has been examined by numerous chemists. The method usually employed for the preparation of this substance is that devised by Zwenger and Dronke (Ann. Suppl. 1, 267), and this was subsequently utilised by Liebermann and Hamburger (Ber. 12, 1179).

Quercitron bark is extracted with 5–6 times its weight of boiling 50 p.c. alcohol, the extract evaporated to one-half, and treated with a little acetic acid, followed by lead acetate solution. The precipitate is removed, sulphuretted hydrogen is passed through the filtrate, and after removal of lead sulphide the clear liquid is evaporated to dryness. The residue is dissolved in a little hot alcohol, the solution treated with water, and the crude quercitrin which separates on cooling is purified by repeated crystallisation from water.

A very convenient source of quercitrin is *yellow flavine* (Perkin, private communication), which consists almost entirely of this substance, and is usually free from quercetin. A hot aqueous extract of this material gives, on cooling, a crystalline precipitate of the glucoside, and this by recrystallisation from water with the aid of animal charcoal is quickly purified.

Quercitrin crystallises in very pale yellow, almost colourless, leaflets, insoluble in cold water, somewhat readily so in alcohol. Aqueous lead acetate gives a bright yellow precipitate. The generally accepted formula for quercitrin is $C_{21}H_{22}O_{12}\cdot 2H_2O_4$ (Herzig, Monatsh. 14, 53), and its hydrolysis with acids into rhamnose (Hlaziwetz and Pfaunder) and quercetin is usually expressed as follows:—

$$C_{21}H_{22}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{14}O_6$$

According to C. W. Moore, however (Proc. Chem. Soc. 1910, 26, 183), the true composition of quercitrin is $C_{21}H_{20}O_{11}\cdot 2H_2O$, and the equation representing its hydrolysis should be as follows:—

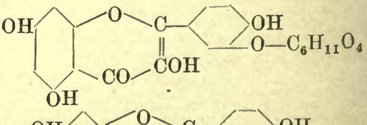
$$C_{21}H_{20}O_{11}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_5$$

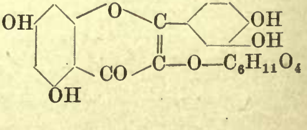
When air-dried quercitron melts at 182°–185°, and in the anhydrous condition at 250°–252°.

It was formerly considered that the glucosides (colouring principles) were hydrolysed during the dyeing operation, and that the shades thus obtained were due not to the glucosides, but to the free colouring matters. This in certain cases is correct, especially when the plant contains an enzyme capable of effecting the hydrolysis: but on the other hand, in many cases the glucoside is itself the colouring matter and directly responsible for the dyeing effect. Quercitrin is an instance in point (Perkin, Chem. Soc. Trans. 1902, 81, 479), and gives upon mordanted fabrics shades which are distinct from those of quercetin itself—

	Chromium	*Aluminium*	*Tin*	*Iron*
Quercitrin	Fullbrown-yellow	Full golden yellow	Lemon yellow	Deep olive
Quercetin	Red-brown	Brown-orange	Bright orange	Orange black
Kaempferol	Brown-yellow	Yellow	Lemon yellow	Deep olive brown

In dyeing property quercitrin very closely resembles kaempferol (*see* Galanga root), and, indeed, differs but little from morin (old fustic) and luteolin (Weld) in this respect. It thus appears probable that the constitution of the glucoside is to be represented by one of the two following formulæ:—





The colours given by quercitrin possess a somewhat faster character than those derived from quercetin.

Commercial Preparations.

Flavin. This is the most important commercial preparation of quercitron-bark; it seems to have been first imported to this country from America. The details of its manufacture have been guarded with much secrecy, and analyses of commercial samples show that different methods have been adopted by different makers. Some specimens consist essentially of quercitrin, and are known as *yellow* flavin, while others contain only quercetin, and are known as *red* flavin. The former have probably been prepared by merely extracting the bark with water and high-pressure steam, or, as it is said, with steam only, at a temperature of 102°–103°.

The best qualities of flavin are those in which the colouring matter is present as more or less pure quercitrin, and entirely free from woody fibre. Red flavin is prepared by rapidly extracting the powdery portion of rasped quercitron bark with ammonia or other alkali, and boiling the solution with sulphuric acid. The precipitate thus produced is ultimately collected, washed with cold water till free from acid, and finally dried. Flavin of this character has about sixteen times the tinctorial value of quercitron-bark. It is not very soluble, but it yields with aluminium and especially with tin mordants, much more brilliant colours than does quercitron bark.

Patent bark, or 'commercial quercetin,' is a preparation of quercitron bark analogous to the garancin made from madder. It is manufactured in a similar manner, viz. by boiling, for about 2 hours, 100 parts finely-ground quercitron bark, 300 parts water, and 15 parts concentrated sulphuric acid. The product is collected on a filter, washed free from acid, and dried. The yield is about 85 p.c. of the bark employed, while its colouring power is much greater. It seems to have been first manufactured in 1855 by Leeshing.

Bark-liquor is simply an aqueous extract of quercitron bark, and is sold with a sp.gr. of 1·66°–1·255°.

Application.—Quercitron bark, patent bark, and bark extracts are chiefly employed by the calico and woollen printer. The latter are used in the preparation of steam-yellows, olives, chocolates, &c., in conjunction with aluminium, tin, chromium, and iron mordants. The former were at one time largely employed in conjunction with garancin, for the production of various compound shades, *e.g.* chocolate, dull red, orange, &c. Now they may be used in a similar manner along with alizarin. When used alone, quercitron bark and patent bark give, with aluminium mordant yellow, with tin orange, with chromium olive-yellow, with iron greenish-olive colours.

Flavin is chiefly used in wool dyeing for the production, in single-bath, of bright yellow and orange, fast to milling, or along with cochineal to obtain a bright scarlet. The mordant employed is stannous chloride and oxalic acid or cream of tartar.

On cotton all the quercitron colours are but moderately fast to light; on wool and silk the chromium, copper, and iron colours are fairly fast, whereas the aluminium and tin colours are only moderately so.

Glucosides of Quercetin.

Rutin was discovered by Weiss (Chem. Zentr. 1842, 305) in the leaves of a rue (*Ruta graveolens* [Linn.]), and was subsequently isolated from capers (*Capparis spinosa* [Linn.]) by Rochleder and Hlasiwetz (Ann. Chem. Pharm. 82, 196), and by Schunck (Manchester Memoirs, 2 Ser. 155, 122, 1858) from buckwheat (*Fagopyrum esculentum* [Moench.]). Whereas Hlasiwetz (Ann. Chem. Pharm. 96, 123) came to the conclusion that rutin was identical with quercitrin, it was shown by Zwenger and Dronke (*ibid.* 123, 145) that this could not be the case, because on hydrolysis rutin gives quercetin and two molecules of sugar. Schunck (Chem. Soc. Trans. 1888, 53, 262; 67, 30) showed that the formula of rutin is $C_{27}H_{32}O_{16},2H_2O$, and that on hydrolysis it is converted into *quercetin* and 2 molecules of rhamnose—

$$C_{27}H_{32}O_{16}+3H_2O=C_{15}H_{10}O_7+2C_6H_{14}O_6$$

Rutin, moreover, was identical with the *sophorin,* which Foerster (Ber. 15, 214) had isolated from the *Sophora japonica.*

It has been shown by Schmidt (Chem. Soc. Trans. 1901, ii. 121) that by the hydrolysis of rutin glucose is also produced, the formula of this substance being, therefore, $C_{27}H_{30}O_{16}$—

$$C_{27}H_{30}O_{16}+3H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6+C_6H_{14}O_6$$

Rutin forms pale yellow glistening needles, sparingly soluble in water, and is said to melt above 190°. With alcoholic potassium acetate it gives a bright yellow *monopotassium salt* (Perkin, Chem. Soc. Trans. 1899, 75, 440).

According to Schmidt, *violaquercitrin* (violarutin) is identical with rutin (*ibid.* 1908, 246, 274), and Perkin (*ibid.* 1910, 97, 1776) has shown that *osyritin* (*Colpoon compressum* (Berg.) [*Osyris compressa*]) (*ibid.* 1902, 81, 477) and *myrticolorin* (*Eucalyptus macrorhyncha* [F. Muell.]) (Smith, *ibid.* 1898, 73, 697) in reality consist of this substance.

The dyeing properties of rutin are similar to, though weaker than those of quercitron bark. The following shades are given on mordanted woollen cloth:—

Chromium	*Aluminium*	*Tin*	*Iron*
Brown-yellow	Full golden yellow	Lemon yellow	Dull brown

Quercimeritrin, $C_{21}H_{20}O_{12}$, yellow plates, m.p. 247°–249°, almost insoluble in boiling water, is contained in cotton flowers (*Gossypium herbaceum*) (Linn.) (Perkin (*ibid.* 1909, 96, 2183), and in the bark of the *Prunus seratina* (Ehrh.) (Finnemore Pharm. Journ. 1910 (iv.) 31, 604). By digestion with boiling dilute sulphuric acid it is hydrolysed according to the equation—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

into quercetin and glucose. On mordanted wool it gives the following shades:—

Chromium	*Aluminium*	*Tin*	*Iron*
Reddish brown	Orange yellow	Bright orange	Olive brown

which are very similar to those given by quercetin itself, and indicate that the sugar is attached to the phloroglucinol nucleus of this colouring matter. *Acetyl quercimeritrin*

$$C_{21}H_{12}O_{10}(C_2H_3O)_8$$

needles, melts at 214°–216°. *Isoquercitrin*

$$C_{21}H_{20}O_{12}$$

is also contained in cotton flowers. It consists of yellow needles, m.p. 217°–219°, and when hydrolysed by acid gives quercetin and glucose—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

It dyes mordanted wool shades which are entirely distinct from those given by quercimeritrin, but closely resemble those yielded by quercitrin, and in this case the sugar group is not attached to the phloroglucinol nucleus of the quercetin molecule.

Chromium	*Aluminium*	*Tin*	*Iron*
Brownish yellow	Golden yellow	Lemon yellow	Brown olive

Incarnatrin $C_{21}H_{20}O_{12},3H_2O$ is present in the 'carnation or crimson' clover, *Trifolium incarnatum* (Linn.) (Rogerson, *ibid.* 1910, 97, 1008), and forms yellow prismatic needles, m.p. 242°–245°. It is hydrolysed by acid according to the following equation :—

$$C_{21}H_{20}O_{12}+H_2O=C_{15}H_{10}O_7+C_6H_{12}O_6$$

into quercetin and a sugar, the osazone of which melts at 203°–205°. It is not identical with quercimeritrin.

Red clover flowers (*Trifolium pratense* [Linn.]) also contain a glucoside of quercetin, which crystallises in yellow needles, m.p. 235°, but as yet has not been completely examined (Power and Salway (*ibid.* 1910, 97, 244).

Other sources of Quercetin.

Heather (*Calluna vulgaris* [Salisb.]) in former times was used as a dyestuff producing a yellow colour upon woollen goods (Crookes, Dyeing and Calico Printing, 1874, 511). Although now almost superseded, it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. It contains *quercetin* (Perkin and Newbury, Chem. Soc. Trans. 1899, 75, 837). According to the late J. J. Hummel, the *Erica tetralix* (bell heather) and the *Erica cinerea* contain only traces of yellow colouring matter. Leuchs (Farben und Färbekunde, 2, 320) refers to the tanning property of heather, and notes that the effect resembles in character that grown by oak bark. According to H. R. Procter it contains 6·4 p.c. of tannin.

White clover (*Trifolium repens* [Linn.]) was at one time employed to a limited extent in country districts for dyeing yellow. A cursory examination of these flowers by Perkin and Phipps (*ibid.* 1904, 85, 58) has indicated the presence of quercetin in the form of glucoside.

Podophyllum Emodi (Wall.) is a small herbaceous plant which grows abundantly in Northern India. The root, or more strictly, the rhizome, has long been used in Indian medical practice, and acts as a powerful purgative. It has been shown by Dunstan and Henry that this rhizome contains *quercetin* in notable amount (*ibid.* 1898, 73, 219), and, according to Hummel (*ibid.*), it compares satisfactorily in dyeing property with quercitron bark. See also articles, ONION SKINS, PERSIAN BERRIES, SOPHORA JAPONICA, CUTCH (*Acacia catechu* and *Uncaria gambier*), and SUMACH (*Osyris compressa, Osyris abysinnica, Ailanthus glandulosa, Rhus rhodanthema, Arctostaphylos uva ursi*). Quercetin has also been shown to exist probably as glucoside in tea leaves (Hlasiwetz and Malin, Jahres. 1867, 732); in the flowers of the horse chestnut (Rochleder, *ibid.* 1859, 523); in the bark of the apple tree (Rochleder, *ibid.* 1867, 731); in *Craetagus oxycantha* (may blossom), and yellow wall-flowers. *Chairanthus chieri* (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1568); *Rumex obtusifolius* (seeds), (Perkin, *ibid.* 1897, 71, 1199), *Delphinium zalil* (Asbarg), (Perkin and Pilgrim, *ibid.* 1898, 73, 381), *Prunus spinosa* (flowers), (Perkin and Phipps, *ibid.* 1904, 85, 56), and *Thespasia lampas* (P. *ibid.* 1909, 95, 1859).

A. G. P.

QUERCYITE *v.* PHOSPHORITE.

QUICKSILVER *v.* MERCURY.

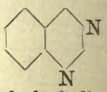
QUIETOL *v.* SYNTHETIC DRUGS.

QUILLAIA SAPOTOXIN *v.* GLUCOSIDES.

QUILLAIC ACID *v.* GLUCOSIDES.

QUINALDINE *v.* QUINOLINE.

QUINAZOLINE, *pheno*-m-*diazine*,



Prepared by treating a strongly cooled alcoholic solution of *o*-formylaminobenzylamine with zinc and dilute hydrochloric acid, precipitating the zinc chloride double salt, converting this into the chromate and decomposing with 33 p.c. aqueous potassium hydroxide. The 3:4-dihydroquinazoline thus formed is oxidised to quinazoline by treatment with potassium ferricyanide in alkaline solution (Gabriel, Ber. 1903, 36, 807; *v.* also Bischler and Lang, Ber. 1895, 28, 292). It forms yellow crystals having a smell like that of naphthalene; m.p. 48–48·5°; b.p. 243°/772·5 mm. The alkylquinazolinium salts with methyl and ethyl halides, prepared by the usual methods for producing quaternary salts, are stated to greatly lower the blood pressure (Gabriel and Colman, D. R. P. 161401, J. Soc. Chem. Ind. 1905, 1031).

QUINCE GUM *v.* GUMS.

QUINIDINE *v.* VEGETO-ALKALOIDS.

QUININE *v.* VEGETO-ALKALOIDS.

QUINIZARIN. 1:4-*Dioxanthraquinone* *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

QUINIZARIN BLUE, GREEN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

QUINOL *v. Hydroquinone*, art. PHENOL AND ITS HOMOLOGUES.

QUINOLCARBOXYLIC ACID *v.* PROTOCATECHUIC ACID.

QUINOLINE. *Leucoline* C_9H_7N.

History.—Quinoline, in an impure form ('leukol'), was isolated first from coal-tar oil of high boiling point by Runge (Pogg. Annalen, 1834, 31, 68). Subsequently, by distilling quinine, cinchonine, or strychnine with caustic potash Gerhardt obtained a basic oil, 'chinolein' (Annalen, 1842, 42, 310; 44, 279), which was shown by Hofmann to be identical with Runge's base (*ibid.* 1843, 47, 76; 1845, 53, 427; *cf.* Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 1). The product from either source is not a pure substance, but a mixture of quinoline with some of its homologues (*cf.* Greville Williams, Chem. Soc. Journ. 1872, 25, 658; Jacobsen and Reimer, Ber. 1883, 16, 1084; Krakau, *ibid.* 1885, 18, 1934). coal-tar quinoline (b.p. 230°–240°) containing 20–25 p.c. of quinaldine (*cf.* Jacobsen, D. R.-P. 23967 of 1882), and, in addition, a noteworthy quantity of *iso*quinoline (Aktieng. für Anilinfab. D. R.-P. 40420 of 1886; Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 125). Quinoline and its homologues also occur in brown coal tar (Doebner, Ber. 1895, 28, 106).

Formation.—The pure base has been obtained by distilling cinchonic acid with lime (Koenigs, Ber. 1879, 12, 98), or cinchonine with a mixture of caustic potash and copper oxide (Wyschnegradsky, *ibid.* 1880, 13, 2318). Synthetically, it can be prepared by the condensation of *o*-aminocinnamic aldehyde (Baeyer and Drewsen, Ber. 1883, 16, 2207), of *o*-aminobenzaldehyde with acetaldehyde (Friedlaender and Göhring, *ibid.* 1835, *v.* p. 473), or of *o*-toluidine with glyoxal (Kulisch, Monatsh. 1894, 15, 277); by passing the vapour of 2-methylindole through a red-hot tube (Pictet, Ber. 1905, 38, 1949), or allylaniline over heated lead oxide (Koenigs, Ber. 1879, 12, 453); by dry distillation of acroleïn-aniline (Koenigs, *ibid.* 1880, 13, 911); or, in about 60 p.c. yield, by heating a mixture of aniline, glycerol, and sulphuric acid with oxidising agents such as nitrobenzene (Skraup, Monatsh. 1880, 1, 317) or arsenic acid (Knueppel, Ber, 1896, 29, 704; D. R.-P. 87334 of 1894).

The formation of quinoline in Skraup's reaction is preceded by condensation of the aniline with acroleïn, produced by dehydration of the glycerol; but it is uncertain whether this initial condensation product, formed in the presence of much acid, is the Schiff's base, acroleïn-aniline (I), as Skraup considered probable, or is an aminoaldehyde (II)—(for Ph, read C_6H_5)—

$$\underset{\text{I}}{Ph\cdot N{:}CH\cdot CH{:}CH_2} \qquad \underset{\text{II}}{Ph\cdot NH\cdot CH_2\cdot CH_2\cdot CHO}$$

as suggested by Blaise and Maire (Compt. rend. 1907, 144, 93; Bull. Soc. chim. 1908, [4] 3, 667; *cf.* Doebner and Miller's synthesis, p. 472).

Preparation.—A mixture of aniline (19 pts.), glycerol (60 pts.) and sulphuric acid (50 pts.), heated by a steam coil to diminish its viscosity, is added slowly to boiling nitrobenzene (12 pts.) in a reflux apparatus, the whole boiled for about 2 hours to complete the reaction, and any unchanged nitrobenzene removed by a current of air. From the product, rendered alkaline with caustic soda, crude quinoline is obtained by distillation with steam and may be freed from the greater part of the unchanged aniline by fractionation. Further purification is effected by oxidation with dichromate mixture, or by treatment with nitrite and acid, followed by distillation from alkaline solution with steam (Skraup, Monatsh. 1881, 2, 141; Walter, J. pr. Chem. 1894, [2] 49, 549). Or, the mixture of aniline, glycerol and sulphuric acid may be boiled with arsenic acid (29 pts.) for 2–3 hours, and the product freed from aniline as just described (Knueppel, *l.c.*).

Properties.—Quinoline is a colourless oily liquid, m.p. −19·5° (Altschul and Schneider, Zeitsch. physikal. Chem. 1895, 16, 24); b.p. 237·1° under 746·8 mm. (Skraup, *l.c.*), 238° under 760 mm. (Kahlbaum; for vapour pressure at each degree between 180° and 240°, *cf.* Young, Chem. Soc. Trans. 1889, 55, 485); sp.gr. 1·1063 at 4°/4°, 1·1018 at 10°/10°, 1·0985 at 15°/15°, 1·0955 at 20°/20° (Perkin, Chem. Soc. Trans. 1896, 69, 1214). It has a disagreeable penetrating odour, a bitter acrid taste, and is very hygroscopic, being converted on exposure to moist air into the *hydrate* $C_9H_7N+1\frac{1}{2}H_2O$ (Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 9), but is only sparingly soluble in water, although dissolved readily by the ordinary organic solvents. It dissolves certain metallic chlorides, bromides and iodides (Walden, Zeitsch. physikal. Chem. 1906, 54, 181), and is soluble in cold alkali bisulphite solutions forming crystallisable compounds which regenerate the base at 60°–70° (Brunck and Graebe, Ber. 1882, 15, 1785).

Reactions.—(1) Quinoline is oxidised only with difficulty by chromic acid mixture (*cf.*, however, de Coninck. Compt. rend. 1898, 128, 682). By potassium permanganate in alkaline solution it is converted into *quinolinic* (pyridine-2 : 3-dicarboxylic) *acid*, oxalic acid, ammonia, and carbon dioxide (Hoogewerff and van Dorp, Ber. 1879, 12, 747, 983; Skraup, Monatsh. 1881, 2, 147).

(2) With chlorine, quinoline forms neither additive nor substitution products. With bromine it gives a *tetrabromide*, decomposing on exposure to the air into the *compound* $B\cdot HBr,Br_2$ (Grimaux, Bull. Soc. chim. 1882, [2] 38, 124), which, when heated, is converted into 3-*bromoquinoline* (Claus and Collischonn, Ber. 1886, 19, 2766). With iodine, the *diiodide*, m.p. 90°, is obtained (Claus and Istel, Ber. 1882, 15, 824), and with iodine chloride the *iodochloride* $B\cdot ClI$, m.p. 159·5° (Pictet and Krafft, Bull. Soc. chim. 1892, [3] 7, 73; Chem. Fab. auf Aktien (vorm. E. Schering), D. R.-P. 30358; Eng. Pat. 9252 of 1884).

(3) By nitration, a mixture of the 5- and 8-*nitroquinolines* or, by further nitration, of the 5 : 7- and 6 : 8-*dinitroquinolines* is obtained (*cf.* Dufton, Chem. Soc. Trans. 1892, 61, 782; Kaufmann and Hüssy, Ber. 1908, 41, 1735).

(4) On sulphonation with anhydrosulphuric acid, quinoline yields a mixture of the 5- and 8-*monosulphonic acids* (*v.* p. 475), or, at higher temperatures, of two *disulphonic acids*.

(5) On reduction with tin (or zinc) and hydrochloric acid, quinoline is converted into the *tetrahydro-* derivative, the four atoms of hydrogen being taken up by the 'pyridine' ring (Wyschnegradsky, Ber. 1879, 12, 1481; 1880, 13, 2400). On further reduction, with hydriodic acid and amorphous phosphorus at 230°, *hexahydroquinoline* and *decahydroquinoline* are obtained in addition to other substances (Bamberger and Lengfeld, Ber. 1890, 23, 1138).

By electrolytic reduction, *tetrahydroquinoline*, 'dihydroquinoline' $(C_9H_9N)_2$, and a polymeride $(C_9H_9N)_3$, are the products (Ahrens, *cf.* Chem. Soc. Abstr. 1897, 72, i. 369; Merck, D. R.-P. 90308 of 1896; 104664; Eng. Pat. 21471 of 1898).

When quinoline is heated with hydrogen and nickel oxide at 240° under 110 atmos., first *tetrahydro-* and then *decahydro-quinoline* are obtained (Ipatiew, Ber. 1908, 41, 992); but when a mixture of quinoline vapour and hydrogen is passed over reduced nickel at 260°–280°, the products are 2-*methylindole*, *methyl-*o*-toluidine*, and o-*toluidine* (Padoa and Carughi, Atti Lincei, 1906, [5] 15, ii. 113).

(6) As a tertiary base, quinoline with alkyl iodides forms quaternary ammonium (quinolinium) compounds, which in alkaline solution

yield 2-alkyl-quinolones mixed with tetrahydro-1-alkylquinolines (*v.* p. 481).

Salts.—As a mono-acid base, quinoline furnishes many salts, but only a few can be mentioned here. The *hydrochloride*, $B{\cdot}HCl+\frac{1}{2}H_2O$, forms deliquescent prisms, m.p. 94°, or, when anhydrous, m.p. 134° (Eckstein, Ber. 1906, 39, 2136); the *chromate*, $B_2{\cdot}H_2Cr_2O_7$, characteristic yellow needles, m.p. 164°–167°, soluble in 275 pts. of water at 10·5° (Hoogewerff and van Dorp, Rec. trav. chim. 1882, 1, 11); the *picrate*, yellow needles, m.p. 203°, from benzene (Goldschmiedt and Schmidt, Monatsh. 1882, 2, 17); the *acid oxalate*, $B{\cdot}C_2H_2O_4$, silky needles; and the *tartrate*, $B_3(C_4H_6O_6)_4$, needles, decomp. 125°, from alcohol (Friese, Ber. 1881, 14, 2805).

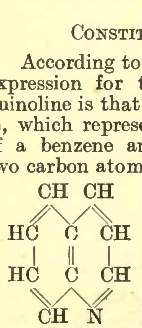
The *platinichloride*, $B_2{\cdot}H_2PtCl_6+2H_2O$, separates from hot dilute hydrochloric acid in orange-yellow needles, m.p. 218° (Lellmann and Alt, Annalen, 1887, 237, 323; *cf.* Eckstein, *l.c.*), soluble in 1200 pts. of cold water; the *aurichloride*, $B{\cdot}HAuCl_4$, yellow, sparingly soluble needles, m.p. 235°–238°, convertible into the 'abnormal' salt $(B{\cdot}HCl)_2AuCl_3$, m.p. 180° (Fenner and Tafel, Ber. 1899, 32, 3227).

Quinoline combines with many salts of heavy metals, forming, in the case of chlorides, crystalline compounds of the type $B{\cdot}HgCl_2$, $B{\cdot}CdCl_2$, &c., which, by hydrochloric acid, are converted into the corresponding double salts, $(B{\cdot}HCl)_2{\cdot}HgCl_2+2H_2O$, $(B{\cdot}HCl){\cdot}CdCl_2+H_2O$, &c., identical with those formed from quinoline hydrochloride and the metallic chloride (Borsbach, Ber. 1890, 23, 431). For summaries of these 'quinolides' and double salts, also of additive compounds, such as $B{\cdot}Br_2$, $(B{\cdot}HCl){\cdot}Br_2$, &c., which quinoline forms with the halogens, reference should be made to Beilstein's Handbuch. The *chloroiodide*, $C_9H_7N{\cdot}ClI$, was at one time proposed as an iodoform substitute under the name 'quinoiodine' (Chem. Fab. auf Aktien. (vorm. E. Schering), D. R.-P. 30358; Eng. Pat. 9252 of 1884).

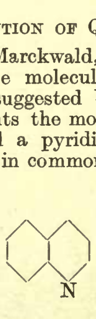
Detection.—For the detection of quinoline, the most sensitive reagent (1 in 25,000) is a solution of potassium iodide (7 grms.) and iodine (5 grms.) in water (100 grms.), which gives a reddish-brown precipitate insoluble in hydrochloric acid; the most characteristic (1 in 3500) is a solution of potassium iodide (5 grms.) and mercuric chloride (1·4 grm.) in water (100 grms.), which produces a yellowish-white precipitate transformed by hydrochloric acid into thin amber-yellow needles (Donath, Ber. 1881, 14, 1771).

CONSTITUTION OF QUINOLINE.

According to Marckwald, the best available expression for the molecular constitution of quinoline is that suggested by Körner (formula I), which represents the molecule as composed of a benzene and a pyridine nucleus having two carbon atoms in common:—



I



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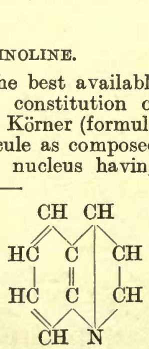
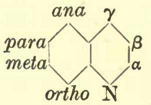


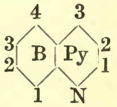
III

Two other formulæ have been suggested, one of them, III, by Riedel, to display the relationship of quinoline to acridine (Ber. 1883, 16, 1609)[1]; and the other by Bamberger to meet objections raised to the alternate single and double linking of the valencies of carbon and nitrogen shown in Körner's formula (Annalen, 1890, 257, 20). But while quinoline in some respects has the properties of an *ortho*-derivative of benzene and of pyridine, in others it shows marked differences from them. It is supposed that these differences arise from the influence of each unsaturated ring system on the other, as they disappear when the unsaturation of one ring is destroyed, *e.g.* by oxidation or by reduction, the product then exhibiting all the characteristics of a derivative of the other (*cf.* Bamberger, *l.c.*).

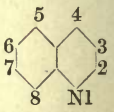
Conventionally, when the object is merely to show the relative position of substituents in the molecule, quinoline is represented by a double hexagon with one side in common, formula II replacing formula I. The orientation of substituents is also indicated by the use of distinctive prefixes, letters, or numerals,[2] thus—



IV



V



VI

System IV was introduced by O. Fischer (Ber. 1884, 17, 755, footnote; *cf.* Skraup, Monatsh. 1886, 7, 157); system V by Baeyer (Ber. 1884, 17, 960); and system VI, which is now the only one recognised, by the Geneva Congress on Nomenclature in 1892 (Chem. News, 65, 280).

Körner's view of the constitution of quinoline finds support in many syntheses of the base or its derivatives, and in the study of the oxidation products of these substances. For example, quinoline and quinaldine have been prepared from *o*-aminobenzaldehyde by condensation with acetaldehyde and with acetone respectively; each, therefore, contains a six-membered carbon ring to which the second ring is attached in the *ortho*- position. When oxidised by permanganate in alkaline solution, quinoline gives pyridine-2 : 3-dicarboxylic (quinolinic) acid (Hoogewerff and van Dorp, Ber. 1879, 12, 747, 983; Skraup, Monatsh. 1881, 2, 147), but quinaldine is converted into acetyl-*o*-aminobenzoic acid (Doebner and Miller, Ber. 1882, 15, 3077).

Orientation in the quinoline series is usually determined by oxidation, with the production either of a substituted phthalic acid, or of a substituted pyridine-2 : 3-dicarboxylic (quinolinic) acid, the constitution of which is known or can be ascertained (*cf.* Miller, Ber. 1890, 23, 2252; 1891, 24, 1900). If, however, disruption of the ring containing the substituent occurs, a synthetical method may afford the information required. For derivatives containing the substituent in the 'benzene' ring, Skraup's synthetical method is invaluable, as the interpretation of the results is free from ambiguity except in the case of syntheses from *meta*- substituted anilines, which may give rise to both *meta*- and *ana*- derivatives of quinoline. Methods for meeting this difficulty have been devised by Skraup and Brunner (Monatsh. 1886, 7, 139), Tortelli (Gazz. chim. ital. 1886, 16, 336), and Lellmann and Alt (Annalen, 1887, 237, 315).

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[1] According to Lellmann two isomeric *ana*- (or 5-) quinolinecarboxylic acids (Annalen, 1887, 237, 325), quinolinesulphonic acids (Ber. 1887, 20, 2172), and quinolinenitriles (Ber. 1888, 21, 397) exist, the isomerism being referred to the presence in the one series, and absence in the other, of the *para*- linking between carbon and nitrogen shown in formula III.

[2] In the publications of the Chemical Society, the positions, starting with the nitrogen atom, were at one time numbered 1′, 2′, 3′, 4′, those in the other ring being numbered 1, 2, 3, 4.

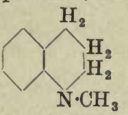
Comparison of the properties of quinoline and naphthalene.—In quinoline, which differs structurally from naphthalene by containing a tervalent nitrogen atom in place of one of the α-methenyl groups, certain of the characteristics of this hydrocarbon are reproduced. Thus, 5-aminoquinoline-4-carboxylic acid yields an internal anhydride (Koenigs and Lossow, Ber. 1899, 32, 717); and lakes are formed by 8-hydroxyquinolines but not by their isomerides (Noelting and Trautmann, *ibid.* 1890, 23, 3660). But the presence of a nitrogen atom in one of the rings destroys the symmetry of the molecule; consequently the number of mono-substitution derivatives becomes seven instead of only two as in naphthalene. Moreover, reactivity, associated in naphthalene with the α- (1-, 4-, 5-, or 8-) position is restricted in quinoline, as in pyridine, to the 2- and 4- positions (*cf. inter alia*, Koenigs, Ber. 1901, 34, 4326; Ephraim, *ibid.* 1891, 24, 2818; 1892, 25, 2706; 1893, 26, 2227; Henrich, *ibid.* 1899, 32, 674), and to these in an approximately equal degree (*cf.* however, Koenigs and Mengel, *ibid.* 1904, 37, 1323).[1]

The orientating effect of the cyclic nitrogen atom in quinoline resembles closely that of the nitro- group in α-nitronaphthalene. For example, each directs the NO_2 or the SO_3H group into both the 5- and the 8- position, this being true also not only of quinoline, but of its derivatives so long as strongly 'positive' (*e.g.* OH or NH_2), or strongly 'negative' (*e.g.* NO_2 or SO_3H) radicles, which themselves exercise a directing influence, are absent from the molecule (Decker and Kaufmann, J. pr. Chem. 1911, [2] 84, 238; Decker and Remfry, Ber. 1905, 38, 2774).

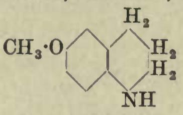
Uses of Quinoline Derivatives.

Quinoline derivatives, in addition to their limited use in the manufacture of dye-stuffs (*v. Cyanines*, p. 481), have found employment as antipyretics and antiseptics. Quinoline and 6-methoxyquinoline are decomposition products of cinchonine and quinine respectively; investigation of the antipyretic properties of these products showed, however, that the specific action which renders quinine so valuable in cases of malaria is not possessed by them (*cf.* Stockmann, J. Physiol. 1894, 15, 245; Fühner, Arch. exp. Path. Pharm. 1906, 55, 27); also that 6-methoxyquinoline, which might be expected to excel quinoline in this respect, is the weaker antipyretic of the two (Jaksch, Prager med. Wochensch. 1881, No. 28).

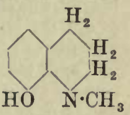
McKendrick and Dewar having shown that reduction (hydrogenation) intensified the physiological effect of bases of the pyridine and quinoline series (Roy. Soc. Proc. 1874, 22, 290), the physiological action of the tetrahydroquinolines was examined, but the results did not fulfil expectation. The best known of these reduction products, kairoline, thalline, and kairine: have marked antipyretic properties—those containing a methyl group in the 1-position being the more valuable (Filehne, quoted, Ber. 1883, 16, 719, 739)—but they all lack the specific properties of quinine.



Kairoline.



Thalline.



Kairine.

The relationship of 4-phenylquinoline to *apo*quinenine, and therefore to the cinchona alkaloids (Koenigs and Nef, Ber. 1886, 19, 2427; Koenigs, *ibid.* 1894, 27, 901; Koenigs and Meimberg, *ibid.* 1895, 28, 1045) led to the investigation of 6-methoxy- and other derivatives of this base (Koenigs and Jaeglé, *ibid.* 1895, 28, 1046; Meister, Lucius & Brüning, D. R.-P. 79173, 79871, 80501 of 1894), but although certain of them are antipyretics, they are useless against malaria, and give rise to dangerous after-effects (*cf.* Mannaberg, Deutsch. Arch. klin. Med. 1897, 59, 185).

Another group of derivatives investigated in this connection are the quinoline analogues of phenacetin. Analgen (8-ethoxy-5-acetylaminoquinoline) and benzanalgen, the benzoyl-derivative, have antipyretic and antirheumatic properties, which are shared by the 6-ethoxy-derivative, but their insolubility in water and uncertainty in action render them useless in medicine.

Quinoline inhibits putrefaction, but not alcoholic fermentation (Donath, Ber. 1881, 14, 1769). Crurin is the bismuth compound of quinoline thiocyanate, for which antiseptic properties have been claimed (Edinger, D. R.-P. 80768, 86251; Eng. Pat. 18516 of 1894; D. R.-P. 86148 of 1895). As iodoform substitutes, vioform (iodo-5-chloro-8-hydroxyquinoline), loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) and other similar compounds have been proposed, but have found no permanent application in surgery.

The following quinophenol derivatives are disinfectants: 'Quinosol,' prepared by heating 8-hydroxyquinoline in alcoholic solution with potassium pyrosulphate, and 'oxyquinaseptol' (diaphtherin) obtained by heating 8-hydroxyquinoline with phenol and diluted sulphuric acid (Lembach and Schleicher, D. R.-P. 73117 of 1892; Eng. Pats. 7803 of 1891; 21968 of 1892).

Syntheses of Quinoline Derivatives.

(i.) *Preparation of derivatives containing radicles substituted in the 'benzene' nucleus.*

Skraup's synthesis. The discovery that not only is quinoline produced by heating aniline with glycerol and sulphuric acid, but that the yield is much increased by the addition of nitrobenzene to the mixture (Skraup, Monatsh. 1880, 1, 317), led to the extension of the method to homologues of aniline either in the presence of the corresponding nitro- derivatives (Skraup, *ibid.* 1881, 2, 139; Schlosser and Skraup, *ibid.* 518), or, for all primary aromatic amines, in that of nitrobenzene (La Coste, Ber. 1882, 15, 558). From *o*- and *p*- substituted anilines, 8- and 6- derivatives of quinolines are respectively obtained, but from *m*- substituted anilines a mixture of the 5- and 7- derivatives is usually formed. In this mixture, one of the isomerides occurs in much larger proportion than the other, bases containing ‘positive’ radicles, *e.g.* *m*-toluidine or *m*-aminophenol, giving chiefly the 7- derivative, but those containing ‘negative’ radicles, *e.g.* *m*-aminobenzoic acid or *m*-aminobenzenesulphonic acid, mainly the 5- derivative.

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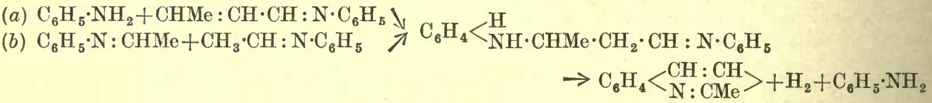
[1] Susceptibility of the methylquinolines to oxidation by chromic acid does not follow this rule, but diminishes in the order 5, 6, 7, 8, 4, 3, 2, the methyl group in the 5- position being the most and that in the 2- position being the least reactive (Miller, Ber. 1890, 23, 2256).

Process.—Except as regards the temperature at which reaction ensues, there is nothing to add to the description of the process given on p. 469. The yields are satisfactory, but the general use of nitrobenzene as an oxidising agent is open to the objection that a certain amount of quinoline will always be formed (*cf.* Skraup, Ber. 1882, 15, 897), and as a substitute, arsenic acid has many advantages (Knueppel, *ibid.* 1896, 29, 704; D. R.-P. 87334 of 1894). Other substitutes are picric acid (Noelting and Trautmann, Ber. 1890, 23, 3663; Kaufmann and Hüssy, *ibid.* 1908, 41, 1739), and the rare earth oxides and sulphates obtained from commercial cerium oxalate (Margosches, J. pr. Chem. 1904, [2] 70, 129).

(ii.) *Preparation of alkyl derivatives containing the alkyl radicle in the ‘pyridine’ ring.*

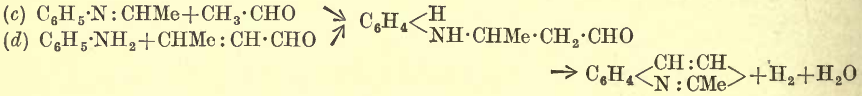
(1) **Doebner and Miller's synthesis.** When glycerol is replaced by glycol in the Skraup reaction, quinaldine is the product (Doebner and Miller, Ber. 1881, 14, 2813), and the same result follows the use of paraldehyde, acetal (*ibid.*), crotonic aldehyde (Skraup, *ibid.* 1882, 15, 897), or lactic acid (Wallach and Wüsten, *ibid.* 1883, 16, 2007). The reaction is due to the conversion of each of these substitutes (except crotonic aldehyde) into acetaldehyde, but the nature of the interaction between aniline and aldehyde in the acid solution has been variously explained. The formation of a Schiff's base with crotonic aldehyde or aldol would lead normally to the production of lepidine instead of quinaldine; therefore it has been supposed that the condensation occurs in the manner represented by the equations (*a*) or (*b*)—leading to the formation of the same intermediate compound—



$$\left.\begin{array}{l}(a)\ C_6H_5{\cdot}NH_2+CHMe:CH{\cdot}CH:N{\cdot}C_6H_5 \searrow\\(b)\ C_6H_5{\cdot}N:CHMe+CH_3{\cdot}CH:N{\cdot}C_6H_5 \nearrow\end{array}\right. C_6H_4<\begin{array}{l}H\\NH{\cdot}CHMe{\cdot}CH_2{\cdot}CH:N{\cdot}C_6H_5\end{array}$$

$$\rightarrow C_6H_4<\begin{array}{l}CH:CH\\N:CMe\end{array}>+H_2+C_6H_5{\cdot}NH_2$$

((*a*) Bischler, Ber. 1892, 25, 2864; (*b*) Miller, *ibid.* 1891, 24, 1720; 1892, 25, 2072; Miller and Plöchl, *ibid.* 1896, 29, 59). On the other hand, it is possible that the unsaturated aldehyde rather than Miller's and Bischler's intermediate compound, which is its anil, is the initial condensation product, its formation being due either (*c*) to an interaction between acetaldehyde-anil and acetaldehyde,[1] or (*d*) to interaction between aniline and crotonic aldehyde (Blaise, and Maire, Bull. Soc. chim. 1908, [4] 3, 667)—



$$\left.\begin{array}{l}(c)\ C_6H_5{\cdot}N:CHMe+CH_3{\cdot}CHO \searrow\\(d)\ C_6H_5{\cdot}NH_2+CHMe:CH{\cdot}CHO \nearrow\end{array}\right. C_6H_4<\begin{array}{l}H\\NH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO\end{array}$$

$$\rightarrow C_6H_4<\begin{array}{l}CH:CH\\N:CMe\end{array}>+H_2+H_2O$$

As quinaldine is formed when a mixture of aniline and aldol is heated with hydrochloric acid (Doebner and Miller, Ber. 1883, 16, 2465), the presence of nitrobenzene is not necessary for the progress of the reaction, which otherwise is similar to that of the Skraup condensation.

The aldol bases produced in reaction (*c*) or (*d*) also undergo condensation when heated at 200°, the product consisting of the quinoline derivative and the corresponding tetrahydrogenated base in molecular proportion (Jones and Evans, Chem. Soc. Trans. 1911, 99, 334). The proportion of the tetrahydro-derivative, however, is not so large when the condensation is effected under the usual conditions, as a portion of the hydrogen shown in the equations is used in reducing the aldehyde to alcohol, which, in the presence of the acid, interacts with the substituted aniline forming a secondary base (Doebner and Miller, Ber. 1884, 17, 1698). The reaction is applicable to all aldehydes of the general formula $CH_2R{\cdot}CHO$ (Miller, Ber. 1885, 18, 3360), or to unsaturated aldehydes of the general formula $CH_2R{\cdot}CH:CR'{\cdot}CHO$, and leads to the production of either 2- or 2:3-derivatives of quinoline, as shown in equation (*b*).

From substituted anilines, such as aminophenols and aminobenzoic acids, quinaldines containing substituents in the ‘benzene’ ring are obtained (Doebner and Miller, Ber. 1884, 17, 939, 1705; Chem. Fab. auf Aktien. (vorm. E. Schering), D. R.-P. 24317 of 1882; Eng. Pat. 956 of 1883; D. R.-P. 29819 of 1883), and with reference to these it may be noted that *m*- substituted anilines seem to give exclusively 7- and not 5- derivatives of quinaldine (Doebner and Miller, Ber. 1883, 16, 2471; Harz, *ibid.* 1885, 18, 3398; *cf.* also Borsche, *ibid.* 1908, 41, 3384).

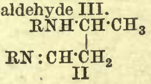
If the aldehyde used in Doebner and Miller's synthesis be replaced by a mixture of a ketone $CH_3{\cdot}CO{\cdot}R$, and an aldehyde in molecular proportion, 4-R-quinoline derivatives are obtained, an unsaturated ketone possibly being formed

---

[1] According to Miller and Plöchl, three products are obtained by the condensation of *m*-xylidine and acetaldehyde, according to the conditions (R being the *m*-xylidinyl radicle), viz. in ethereal solution the Schiff's base I; in warm aqueous solution its polymeride II; in hydrochloric acid solution its condensation product with acetaldehyde III.

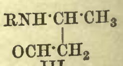
$CH_3{\cdot}CH:NR$

I



$$\begin{array}{l}RNH{\cdot}CH{\cdot}CH_3\\ \qquad\quad |\\ RN:CH{\cdot}CH_2\end{array}$$

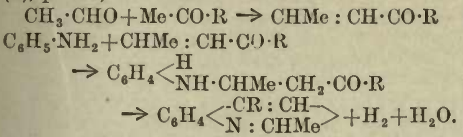
II



$$\begin{array}{l}RNH{\cdot}CH{\cdot}CH_3\\ \qquad\quad |\\ OCH{\cdot}CH_2\end{array}$$

III

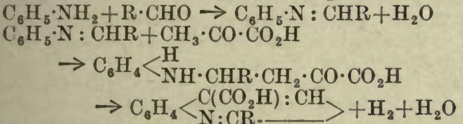
as an intermediate product (*cf.* equation (*d*), p. 472)[1]—



$$\mathrm{CH_3\cdot CHO+Me\cdot CO\cdot R \rightarrow CHMe:CH\cdot CO\cdot R}$$
$$\mathrm{C_6H_5\cdot NH_2+CHMe:CH\cdot CO\cdot R}$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{H}\\ \mathrm{NH\cdot CHMe\cdot CH_2\cdot CO\cdot R}\end{matrix}\right.$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{-CR:CH-}\\ \mathrm{N:CHMe}\end{matrix}\right>\mathrm{+H_2+H_2O.}$$

(Beyer, J. pr. Chem. 1885, [2] 31, 48; 32, 127; 1886, [2] 33, 395).

A similar condensation, with the production of derivatives of quinoline-4-carboxylic (cinchonic) acid, ensues when pyruvic acid, an aldehyde and aniline are warmed together in alcoholic solution (Böttinger, Annalen, 1878, 191, 321; Doebner, *ibid.* 1887, 242, 270; 1888, 249, 98; Pictet and Misner, Ber. 1912, 45, 1801). The course of this reaction may be represented thus (*cf.* equation (*c*), p. 472)—

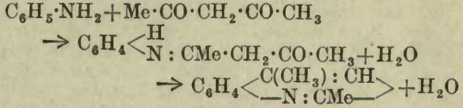


$$\mathrm{C_6H_5\cdot NH_2+R\cdot CHO \rightarrow C_6H_5\cdot N:CHR+H_2O}$$
$$\mathrm{C_6H_5\cdot N:CHR+CH_3\cdot CO\cdot CO_2H}$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{H}\\ \mathrm{NH\cdot CHR\cdot CH_2\cdot CO\cdot CO_2H}\end{matrix}\right.$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{C(CO_2H):CH}\\ \mathrm{N:CR\text{-}\!\!-\!\!-\!\!-}\end{matrix}\right>\mathrm{+H_2+H_2O}$$

(Simon and Mauguin, Compt. rend. 1907, 144, 1275; Borsche, Ber. 1908, 41, 3886).

Process.—To prepare quinoline derivatives by Doebner and Miller's method, aniline or the substituted aniline is mixed with twice its weight of fuming hydrochloric acid, and the requisite quantity of aldehyde added gradually, care being taken to avoid rise of temperature. If a β-hydroxyketone is to be used, the mixture of ketone and aldehyde required for its production must be polymerised by means of hydrogen chloride before it is added gradually to the mixture of aniline and hydrochloric acid. After being heated for many hours on a water-bath, the product is digested with water, the filtrate rendered alkaline by caustic soda solution, the precipitated base freed from secondary amines by treatment in acid solution with nitrite, and the quinoline derivative purified, either by fractional distillation or by conversion into the sparingly soluble crystalline picrate (*cf.* Harz, Ber. 1885, 18, 3384; Miller and Kinkelin, *ibid.* 1886, 19, 527; Schultz, *ibid.* 1883, 16, 2600; 1884, 17, 1965; Actieng. für Anilinfab., D. R.-P. 28217; Eng. Pat. 4207 of 1883; Beyer, J. pr. Chem. 1886, [2] 33, 401; Reed, *ibid.* 1887, [2] 35, 299; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 35133 of 1885).

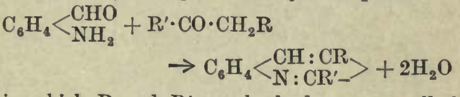
(2) **Beyer's synthesis.** In the Doebner and Miller reaction both hydrogen and water are eliminated in the condensation. If a β-diketone is used instead of the β-hydroxyaldehyde or β-hydroxyketone, hydrogen ceases to be one of the products, and the yield of quinoline derivative is improved. To bring about the condensation, the product obtained by heating a mixture of aniline and the diketone in molecular proportion is warmed for some hours with concentrated hydrochloric acid:



$$\mathrm{C_6H_5\cdot NH_2+Me\cdot CO\cdot CH_2\cdot CO\cdot CH_3}$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{H}\\ \mathrm{N:CMe\cdot CH_2\cdot CO\cdot CH_3+H_2O}\end{matrix}\right.$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{C(CH_3):CH}\\ \mathrm{-N:CMe-}\end{matrix}\right>\mathrm{+H_2O}$$

(Beyer, Ber. 1887, 20, 1770; Combes, Compt. rend. 1888, 106, 142; 1889, 108, 1252).

(3) **Friedlaender's synthesis.** The elimination of hydrogen is avoided also if, instead of aniline and a diketone, a mixture of an *o*-keto-substituted aniline and either an aldehyde or a ketone is used, the condensation proceeding with such readiness that the interacting substances need only be dissolved in water or aqueous alcohol, and warmed with a few drops of dilute caustic soda solution. With *o*-aminobenzaldehyde, the reaction may be represented by the equation—

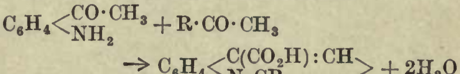


$$\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CHO}\\ \mathrm{NH_2}\end{matrix}\right.\mathrm{+R'\cdot CO\cdot CH_2R}$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CH:CR}\\ \mathrm{N:CR'-}\end{matrix}\right>\mathrm{+2H_2O}$$

in which R and R′ can be hydrogen or alkyl radicles. As in the Doebner and Miller reaction, an aldol polymerisation probably ensues as an intermediate stage (Friedlaender, Ber. 1882, 15, 2574; Friedlaender and Göhring, *ibid.* 1883, 16, 1835; 1884, 17, 456).

From *o*-aminoacetophenone or *o*-aminobenzophenone and methyl alkyl ketones, under similar conditions, derivatives of 4-methyl- or 4-phenyl-quinoline can be produced (Geigy and Koenigs, Ber. 1885, 18, 2406; O. Fischer, *ibid.* 1886, 19, 1037).

Isatic acid also interacts similarly with ketones, their *iso*nitroso- derivatives, ketonic acids or aldoximes, furnishing derivatives of quinoline-4-carboxylic (cinchonic) acid—



$$\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CO\cdot CH_3}\\ \mathrm{NH_2}\end{matrix}\right.\mathrm{+R\cdot CO\cdot CH_3}$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{C(CO_2H):CH}\\ \mathrm{N:CR\text{-}\!\!-\!\!-\!\!-}\end{matrix}\right>\mathrm{+2H_2O}$$

(Pfitzinger, J. pr. Chem. 1885, [2] 33, 100; 1888, [2] 38, 582; 1897, [2] 56, 283; 1902, [2] 66, 263; Hübner, Ber. 1906, 39, 982).

(iii.) *Methods which give rise to the production of hydroxyquinolines containing the hydroxyl radicle in the 'pyridine' ring.*

The direct introduction of hydroxyl into the 'pyridine' ring of quinoline has been accomplished only in a few cases, such as the formation of carbostyril (2-hydroxyquinoline) by the action of hypochlorous acid on quinoline (Einhorn and Lauch, Ber. 1886, 19, 53; Erlenmeyer and Rosenhek, *ibid.* 1885, 18, 3295; 1886, 19, 498). Synthetical methods, however, have been devised for the production of 2- and 4-hydroxyquinolines, the most important of them being modifications of condensations already described.

From ethyl acetoacetate, derivatives of either 2-hydroxyquinoline or 4-hydroxyquinoline can be obtained by condensation with aniline, according as the anilide or the β-phenylamino-crotonate forms the intermediate product.

(1) **Knorr's synthesis.** The anilide, formed when a mixture of ethyl acetoacetate and aniline in molecular proportion is heated at 120°–150° under pressure for many hours,

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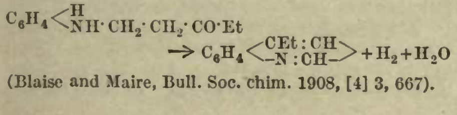
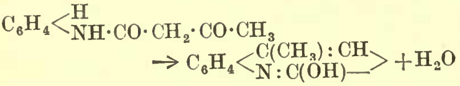
[1] This view of the reaction is supported by the known behaviour of β-anilinoethyl ethyl ketone when heated with aniline hydrochloride



$$\mathrm{C_6H_4}\left<\begin{matrix}\mathrm{H}\\ \mathrm{NH\cdot CH_2\cdot CH_2\cdot CO\cdot Et}\end{matrix}\right.$$
$$\rightarrow \mathrm{C_6H_4}\left<\begin{matrix}\mathrm{CEt:CH}\\ \mathrm{-N:CH-}\end{matrix}\right>\mathrm{+H_2+H_2O}$$

(Blaise and Maire, Bull. Soc. chim. 1908, [4] 3, 667).

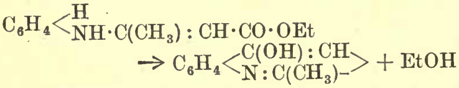
corresponds in structure with that of the intermediate compounds occurring in the Skraup and the Doebner and Miller syntheses. To effect the condensation to the carbostyril derivative, concentrated sulphuric acid is used either in the cold or at the temperature of a water-bath, the product afterwards being stirred into water and rendered alkaline with caustic soda—



$$C_6H_4<\begin{array}{l}H\\NH\cdot CO\cdot CH_2\cdot CO\cdot CH_3\end{array} \rightarrow C_6H_4<\begin{array}{l}C(CH_3):CH\\N:C(OH)—\end{array}> + H_2O$$

The method gives good yields (Knorr, Annalen, 1886, 236, 75, 83; D. R.-P. 26428 of 1883),[1] and may be applied to substituted anilines, homologues of aniline or mono-alkyl derivatives of ethyl acetoacetate (Knorr, Annalen, 1888, 245, 358), but secondary anilines, such as methylaniline and its homologues react with ethyl acetoacetate forming lepidone-(2-keto-tetrahydroquinoline-) derivatives (Knorr, *ibid.* 1886, 236, 106; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 32281 of 1884).

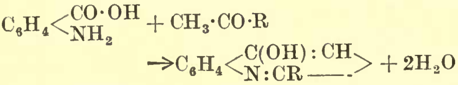
(2) **Conrad and Limpach's synthesis.** The β-aminocrotonate, obtained by the interaction of ethyl acetoacetate and aniline or its homologues in molecular proportion in the cold, is converted into the 4-hydroxyquinoline by rapidly heating it to 240°–250°. By extraction of the product with dilute acid, the hydroxyquinoline can be separated from the lutidone-carboxylic acid which is also formed in the condensation.



$$C_6H_4<\begin{array}{l}H\\NH\cdot C(CH_3):CH\cdot CO\cdot OEt\end{array} \rightarrow C_6H_4<\begin{array}{l}C(OH):CH\\N:C(CH_3)-\end{array}> + EtOH$$

The yields are only moderate (Conrad and Limpach, Ber. 1887, 20, 947; 1888, 21, 523, 1649, 1968; 1891, 24, 2990; D. R.-P. 42276 of 1887; Knorr, Ber. 1887, 20, 1397).

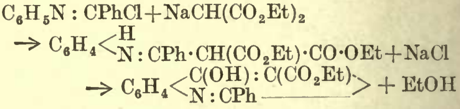
(3) Friedlaender's reaction described under ii. (3) finds its analogue in the condensation of anthranilic acid with ketones or ketonic esters under the influence of heat—



$$C_6H_4<\begin{array}{l}CO\cdot OH\\NH_2\end{array} + CH_3\cdot CO\cdot R \rightarrow C_6H_4<\begin{array}{l}C(OH):CH\\N:CR——\end{array}> + 2H_2O$$

Owing to the conversion of some of the anthranilic acid into aniline, other products are also formed, the yield of hydroxyquinolines being only moderate (Niementowski, Ber. 1894, 27, 1394; Niementowski and Orzechowski, *ibid.* 1895, 28, 2809; Niementowski, *ibid.* 1905, 38, 2044; 1907, 40, 4285). The condensation of acetyl-*o*-aminoacetophenone, effected by alcoholic caustic soda solution in the cold, is also a reaction of this type, but, as in the acetoacetate syntheses, both the 2-hydroxy-4-methyl- and the 4-hydroxy-2-methyl-quinolines are formed (Bischler and Howell, Ber. 1893, 26, 1397; Camps, *ibid.* 1899, 32, 3228; Arch. Pharm. 1899, 237, 659; 1901, 239, 591; 1902, 240, 659).

(4) From benzanilide, or its homologues, 4-hydroxyquinoline derivatives can be obtained by heating the product formed by the interaction of the derived imino-chloride and ethyl sodiomalonate or sodioacetoacetate in molecular proportion, and afterwards eliminating carbon dioxide from the resulting 4-hydroxyquinoline-3-carboxylate—



$$C_6H_5N:CPhCl+NaCH(CO_2Et)_2 \rightarrow C_6H_4<\begin{array}{l}H\\N:CPh\cdot CH(CO_2Et)\cdot CO\cdot OEt\end{array}+NaCl \rightarrow C_6H_4<\begin{array}{l}C(OH):C(CO_2Et)\cdot\\N:CPh——\end{array}> + EtOH$$

(Just, Ber. 1885, 18, 2632; 1886, 19, 979, 1462, 1541; D. R.-P. 33497 of 1885).

HALOGEN DERIVATIVES.

Chloroquinolines are not produced by direct substitution, but can be obtained—

(1) From chloroanilines by Skraup's method. The product from *m*-chloroaniline is a mixture of the 5- and 7-chloroquinolines (La Coste, Ber. 1885, 18, 2941).

(2) From aminoquinolines by the Sandmeyer reaction (*cf.* Wenzel, Monatsh. 1894, 15, 459).

(3) From hydroxyquinolines by interaction with phosphorus pentachloride (*cf.* Friedlaender and Ostermaier, Ber. 1882, 15, 333).

All seven monochloro-, and many di- and tri-chloro-quinolines are known. The mono-derivatives are oils or have a low melting-point; they are less basic than quinoline, the decrease in basicity being most marked in the 2- compound; and they furnish additive compounds with alkyl iodides. The halogen is reactive only in the 2- or 4- position.

Bromoquinolines can be obtained by direct substitution or by suitable modifications of the processes applicable to the chloro- compounds. The seven monobromoquinolines are known, their properties being similar to those of the corresponding chloro- derivatives.

NITROQUINOLINES.

The mononitration of quinoline is achieved by adding alternately quinoline nitrate and anhydrosulphuric acid of sp.gr. 2·0 to concentrated sulphuric acid (Dufton, Chem. Soc. Trans. 1892, 61, 793; *cf.* Koenigs, Ber. 1879, 12, 449; Claus and Kramer, *ibid.* 1885, 18, 1243; Noelting and Trautmann, *ibid.* 1890, 23, 3654). The 5- and 8-nitroquinolines, produced together with some dinitrohydroxyquinoline, can be separated as the 5-isomeride forms a nitrate sparingly soluble in dilute nitric acid (Dufton, *l.c.*); or is converted into a quaternary compound by methyl sulphate (Decker, Ber. 1905, 38, 1154). Further nitration converts the 5-nitro- and 8-nitro- into the 5 : 7- and 6 : 8-dinitroquinolines respectively; but the 6-nitro- (obtained by Skraup's method) into a mixture of the 5 : 6- and 6 : 8-dinitro-, also the 7-nitro- (obtained by Skraup's method) into a mixture of the 5 : 7- and 7 : 8- dinitro-quinolines (Kaufmann and Decker, Ber. 1906, 39, 3648; Kaufmann and Hüssy, *ibid.* 1908, 41, 1735). Trinitro- derivatives have not been described.

The nitroquinolines are crystalline; they dissolve in concentrated mineral acids, but their basic properties are feeble, and the salts are mostly decomposed by water. In many cases they form quaternary ammonium compounds with methyl iodide.

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[1] By this method, hydroxy-6 : 8-dimethylquinolines have been prepared, one of which is closely related to the alkaloid cytisine (Ewins, Chem. Soc. Trans. 1913, 103, 100; *cf.* Ewins and King, *ibid.* 104).

AMINOQUINOLINES.

Of the aminoquinolines, six have been described. Those containing the NH_2 group in the 'benzene' ring can be obtained, either by reduction of the corresponding nitro- derivatives with tin and hydrochloric acid, or, like those containing it in the 'pyridine' ring, by heating the corresponding hydroxyquinoline with ammonio-zinc chloride.

2-Aminoquinoline is obtained by heating 2-chloroquinoline with ammonium carbonate and ammonia at 210° (Claus and Schaller, J. pr. Chem. 1897, [2] 56, 206), and from *o*-aminocinnamonitrile $NH_2 \cdot C_6H_4 \cdot CH : CH \cdot CN$, by interaction with sodium ethoxide (Pschorr, Ber. 1898, 31, 1289). 4-Aminoquinoline can be prepared from cinchonamide by Hofmann's method (Wenzel, Monatsh. 1894, 15, 457). 3-Aminoquinoline has not been described.

The aminoquinolines are crystalline compounds, which act usually as mono- acid bases, give quaternary ammonium compounds with alkyl iodides, and are diazotisable, resembling in this respect primary aromatic amines.

QUINOLINESULPHONIC ACIDS.

On sulphonation with concentrated sulphuric acid at 220°–230°, quinoline yields the 8-sulphonic acid, but after many hours at 275°–280°, the 6-sulphonic acid (Georgievics, Monatsh. 1887, 8, 577, 639; Bad. Anilin- & Soda-Fab., D. R.-P. 40901 of 1887), both the 5- and the 8-sulphonic acids being converted into the 6-acid under these conditions (*ibid.*; Lellmann and Reusch, Ber. 1889, 22, 1391).

The 5- and 8- acids are obtained, but in proportions which depend on the temperature and concentration of the acid, when quinoline is heated with anhydrosulphuric acid at 120°–200°; the 8- acid predominates at lower, and the 5- acid at higher temperatures (Bedall and O. Fischer, Ber. 1882, 15, 683, 1979;[1] Riemerschmied, *ibid.* 1883, 16, 721; La Coste and Valeur, *ibid.* 1887, 20, 95). According to Claus, a third acid, the 7-sulphonic acid, is also present in the product at 125°–130°, but disappears as the temperature is raised (J. pr. Chem. 1888, [2] 37, 261). By further sulphonation with Nordhausen acid at 250°, a mixture of two disulphonic acids is produced (La Coste and Valeur, *l.c.*; La Coste, D. R.-P. 29920 of 1884.

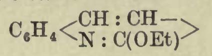
For the preparation of the 5- acid, Skraup's method can be used (Lellmann and Lange, Ber. 1887, 20, 1446), and, by comparison of this acid with the 5- acid obtained by sulphonation under different conditions, Lellmann has drawn the conclusion that the latter exists in two forms (*ibid.* 2172; *cf.* Jakubowski, *ibid.* 1910, 43, 3026).

The quinolinesulphonic acids are crystalline, and can be separated from mixtures by fractional crystallisation of the calcium salts. They yield hydroxyquinolines by fusion with caustic alkali; nitriles by distillation with potassium cyanide; and di- or tri-bromoquinolines, with loss of the SO_3H group, on bromination in aqueous solution.

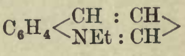
HYDROXYQUINOLINES.

Six of the seven hydroxyquinolines are known, viz. the 2- and 4- derivatives, and the four quinophenols, containing the OH group in the 'benzene' ring. From each, by combination with alkyl iodides, quaternary ammonium compounds are obtained.

The 2- and 4-hydroxyquinolines are produced either by synthetical methods (*v.* p. 473) or from the corresponding chloroquinolines by interaction with water at 120°. They exhibit the properties both of hydroxy- compounds and of ketonic derivatives, forming, for example, two series of ethers—



$$C_6H_4 < \begin{matrix} CH : CH - \\ N : C(OEt) \end{matrix} >$$



$$C_6H_4 < \begin{matrix} CH : CH \\ NEt : CH \end{matrix} >$$

are less basic than the quinophenols; and are not reduced by tin and hydrochloric acid, but, in boiling alcoholic solution with sodium, eliminate the OH group forming tetrahydroquinoline.

The isomeric quinophenols can be prepared from aminophenols by Skraup's reaction; from aminoquinolines by the diazo- reaction; or from quinolinesulphonic acids by fusion with caustic alkali. They resemble the phenols or naphthols in properties, give only one series of ethers on alkylation, yield nitro- derivatives and sulphonic acids, and furnish stable salts with acids or alkalis. The 6- and 8-hydroxyquinolines, moreover, give nitroso- derivatives with nitrous acid, and couple with diazotised bases forming azo- dyes.

(i.) **2-Hydroxyquinoline** (*Carbostyril*) is obtained when ethyl *o*-nitrocinnamate is reduced with alcoholic ammonium sulphide (Friedlaender and Ostermaier, Ber. 1881, 14, 1916); when *o*-aminocinnamic acid is boiled for some hours with hydrochloric acid (Tiemann and Oppermann, *ibid.* 1880, 13, 2070), or 50 p.c. sulphuric acid (Feer and Koenigs, *ibid.* 1885, 18, 2395); when 2-chloroquinoline is heated with water at 120° (Friedlaender and Ostermaier, *ibid.* 1882, 15, 335) or when quinoline is left in contact with bleaching-powder solution containing boric acid for some days (Erlenmeyer and Rosenhek, *ibid.* 1885, 18, 3295; Einhorn and Lauch, *ibid.* 1886, 19, 53); and, in 80 p.c. yield, when acetyl-*o*-aminobenzaldehyde in dilute (10 p.c.) alcoholic solution is boiled with one-third its weight of caustic soda (Camps, Arch. Pharm. 1899, 237, 682). Its occurrence in a sublimate collected from a furnace used for the ignition of sugar liquors has been noted by Lippmann (Ber. 1905, 38, 3829).

Properties.—It crystallises in prisms, or, from dilute aqueous solution with 1 mol. H_2O in needles, m.p. 199°–200°, is only sparingly soluble in cold water, and insoluble in ammonia, but dissolves in hydrochloric acid or caustic alkali solution. In many of its reactions, it has the properties of a phenol, in others those of a ketone (*cf.* Hartley and Dobbie, Chem. Soc. Trans. 1899, 75, 646); the corresponding ethers are known, the C-*methyl ether*, b.p. 246°–247° (Friedlaender and Weinberg, Ber. 1882, 15, 1422), and the N-*methyl ether* (1-methyl-2-quinolone), m.p. 74°, b.p. 324° (Friedlaender and

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[1] The 'meta'- acid described in these communications is the 5- not the 7- acid.

Müller, *ibid.* 1887, 20, 2009). On oxidation with alkaline permanganate, it yields *isatin* and *carbostyrilic* (oxalylanthranilic) *acid* (Friedlaender and Ostermaier, Ber. 1882, 15, 332); and on reduction in boiling alcohol with sodium it gives *tetrahydroquinoline* (Knorr and Klotz, *ibid.* 1886, 19, 3302).

(ii.) **4-Hydroxyquinoline** (*Kynurine*), first obtained from kynurenic acid by sublimation (*cf.* Schmiedeberg and Schultzen, Annalen, 1872, 164, 158), occurs among the oxidation products of cinchonine, cinchonidine, and cinchonic acid (Skraup, Monatsh. 1886, 7, 518; 1888, 9, 801, 818; 1889, 10, 726), and has been synthesised from cinchonamide (Wenzel, *ibid.* 1894, 15, 453), from 4-chloroquinoline by heating it with water at 120° (Skraup, *ibid.* 1889, 10, 726), and from formyl-*o*-aminoacetophenone by boiling it with caustic soda solution (Camps, Ber. 1901, 34, 2709).

Properties.—It forms prisms, m.p. 201°, or, if rapidly separated from solution, needles (with 3 mol. H_2O), dissolves readily in warm water, alcohol or ether, and gives in aqueous solution a carmine colouration with ferric chloride. The *hydrochloride* $B \cdot HCl + 2H_2O$, and *platinichloride* $B_2 \cdot H_2PtCl_6 + 2H_2O$, crystallise in needles. Like carbostyril, it forms both *O*- and *N*- ethers (Wenzel, *l.c.*; H. Meyer, Monatsh. 1906, 27, 255, 987).

The 3-carboxylic acid (*kynurenic acid*) occurs in the urine of dogs fed on par-boiled meat (Liebig, Annalen, 1853, 86, 125; 1858, 108, 354; *cf. inter alia*, Kretschy, Monatsh. 1881, 2, 58; Ellinger, Ber. 1904, 37, 1807), and has been synthesised by boiling ethyl formyl-*o*-aminophenylpropiolate with caustic soda solution (Camps, Ber. 1901, 34, 2714). It forms prisms, $HA + H_2O$, melts, when anhydrous, at 257°–258°, and is only sparingly soluble in hot water. On oxidation with alkaline permanganate it yields *oxalylanthranilic acid* (Kretschy, Monatsh. 1884, 5, 16).

(iii.) **5-Hydroxyquinoline,** obtained by fusing quinoline-5-sulphonic acid with caustic alkali (Riemerschmied, Ber. 1883, 16, 721; Lellmann, *ibid.* 1887, 20, 2174), forms scales, m.p. 224°.

The 8-sulphonic acid is converted, by means of potassium iodide and hypochlorous acid, into the 6-*iodo*-5-*hydroxyquinoline*-8-*sulphonic acid* (Claus, J. pr. Chem. 1896, [2] 53, 339; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 89600 of 1895).

(iv.) **6-Hydroxyquinoline** can be prepared from *p*-aminophenol by Skraup's reaction (Skraup, Monatsh. 1882, 3, 545; D. R.-P. 14976; Eng. Pat. 678 of 1881); or by fusing quinoline-6-sulphonic acid with caustic alkali (O. Fischer and Willmack, Ber. 1884, 17, 440; Happ, *ibid.* 191; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 26430 of 1883). It forms prisms, m.p. 193°, which dissolve only very sparingly in cold water.

Reactions.—(1) With nitrous acid, it gives the 5-*nitroso*- derivative (the 5-oxime of quinoline-5 : 6-quinone), convertible by hydroxylamine into the 5 : 6-*dioxime* which forms lakes with mordants (*cf.* Mathëus, Ber. 1888, 21, 1886; Kostanecki and Reicher, *ibid.* 1891, 24, 158).

(2) It couples with diazotised bases forming *azo*- dyes (Mathëus, Ber. 1888, 21, 1642).

(3) Its potassium salt, heated with carbon dioxide under pressure at 170°, yields *potassium* 6-*hydroxyquinolinecarboxylate* (Schmitt and Altschul, Ber. 1887, 20, 2695).

The methoxy- derivative (6-*quinanisole*), obtained either by the Skraup reaction (Skraup, Monatsh. 1885, 6, 762; Bad. Anilin- & Soda-Fab. D. R.-P. 28324 of 1883), or by methylating 6-hydroxyquinoline (Skraup, Monatsh. 1882, 3, 544), is an oil, b.p. 304°–305° (slight decomp.) under 740 mm., sp.gr. 1·1542 at 20°. Its salts, like those of quinine, show blue fluorescence in aqueous solution, and with chlorine water and ammonia give a green colouration. On reduction with tin and hydrochloric acid it furnishes *thalline* (Bad. Anilin- & Soda-Fab. D. R.-P. 30426 of 1884).

For 5-iodo-6-hydroxyquinoline, *see* Claus, D. R.-P. 78880 of 1894.

6-Ethoxyquinoline, b.p. 290°–292°, on nitration, gives tho 5-*nitro*- derivative, needles, m.p. 111°. This, when reduced, yields the 5-*amino*- derivative, needles, m.p. (anhydrous) 115°–116°, which forms an *acetyl* derivative, scales, m.p. 163°, and a *benzoyl* derivative, m.p. 144° (Vis, J. pr. Chem. 1893, [2] 48, 29; Dahl & Co., D. R.-P. 69035 of 1891).

(v.) **7-Hydroxyquinoline,** obtained either from *m*-aminophenol by the Skraup reaction (Skraup, Monatsh. 1882, 3, 559), or by fusing quinoline-7-sulphonic acid with caustic alkali (O. Fischer, Ber. 1882, 15, 1979), crystallises in prisms, m.p. 235°–238°, is less soluble than the 6-isomeride in water, and in solution shows green fluorescence.

(vi.) **8-Hydroxyquinoline** (*Quinophenol*) is prepared either from *o*-aminophenol by the Skraup reaction (Skraup, Monatsh. 1882, 3, 536; D. R.-P. 14976; Eng. Pat. 678 of 1881), or from quinoline-8-sulphonic acid by fusion with caustic alkali (Bedall and O. Fischer, Ber. 1881, 14, 443, 1366). It forms prismatic needles, m.p. 76°, b.p. 266·6° (corr.) under 752 mm. (Skraup), dissolves only very sparingly in cold water, but readily in alcohol, and, unlike its isomerides, is volatile with steam. The aqueous solutions of its acid or alkali salts are yellow.

Reactions.—(1) By methylation, it is converted into the 8-*quinanisole*, an oil, b.p. 265°–268° (Bedall and O. Fischer, *l.c.*), which can also be obtained by the Skraup reaction from *o*-anisidine (Skraup, Monatsh. 1882, 3, 544).

(2) With nitrous acid, it furnishes the 5-*nitroso*- derivative (the 5-oxime of quinoline-5 : 8-quinone), convertible by hydroxylamine into the 5 : 8-*dioxime* which forms lakes with mordants (Lippmann and Fleissner, Monatsh. 1889, 10, 794; Kostanecki, Ber. 1891, 24, 151).

(3) It couples with diazotised bases, forming *azo*- dyes (Mathëus, Ber. 1888, 21, 1644).

(4) When its sodium salt is heated with carbon dioxide at 140°–150° under pressure, *sodium* 8-*hydroxyquinolinecarboxylate* is obtained (Schmitt and Engelmann, Ber. 1887, 20, 1217, 2690; *cf.* Heyden, D. R.-P. 39662; Eng. Pat. 10280 of 1886).

(5) By interaction with ω-bromacetophenone in presence of alcoholic caustic alkali solution, it yields *acetophenone-8-hydroxyquinoline* (Zimmer & Co., D. R.-P. 92755 of 1895).

Iodochloro-8-hydroxyquinoline (Basler chem. Fab. D. R.-P. 117767 of 1899; Eng.

Pat. 3915 of 1900); 5:6-diiodo-8-hydroxyquinoline (Claus, D. R.-P. 78880 of 1894); 7-iodo-8-hydroxyquinoline-5-sulphonic acid (Claus, D. R.-P. 72942 of 1892; Griese, D. R.-P. 190956 of 1906; Eng. Pat. 9656 of 1905) and similar compounds (*cf.* Claus, D. R.-P. 73145 of 1893; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 84063 of 1895) have been proposed as iodoform substitutes.

8-Ethoxyquinoline, obtained by heating 8-hydroxyquinoline with ethyl bromide and alcoholic caustic soda (O. Fischer and Renouf, Ber. 1884, 17, 759; Vis, J. pr. Chem. 1892, [2] 45, 531), needles, b.p. 285°–287°, forms *5-nitro-8-ethoxyquinoline*, m.p. 128°, on nitration with nitric acid of sp.gr. 1·52. From the corresponding *5-amino-* derivative, scales, m.p. 114°, an *acetyl* derivative, analgen (the phenacetin of the quinoline series), needles, m.p. 155°, and a *benzoyl* derivative, benzanalgen, a crystalline powder, m.p. 206°, have been obtained (Vis, *l.c.*; D. R.-P. 60308 of 1891; Dahl & Co., D. R.-P. 65102; Eng. Pat. 17493 of 1891; D. R.-P. 65111; Eng. Pat. 3147 of 1892). The corresponding *acetyl-5-amino-8-methoxyquinoline* forms needles, m.p. 178°–179° (Vis, J. pr. Chem. 1893, [2] 48, 24; Dahl & Co., D. R.-P. 65110 of 1892).

8-Hydroxyquinoline-5-sulphonic acid, prepared by sulphonating 8-hydroxyquinoline with cooled anhydrosulphuric acid (Claus and Posselt, J. pr. Chem. 1890, [2] 41, 33) has been used as an antiseptic under the name quinosol (Fritzsche, D. R.-P. 88520 of 1895; Eng. Pat. 1409 of 1896; D. R.-P. 187943 of 1905; 187869; Eng. Pat. 11725 of 1906). For its physiological action, *cf.* Brahms, Zeitsch. physiol. Chem. 1899, 28, 439.

2:4-Dihydroxyquinoline (*γ-hydroxycarbostyril*) is the only dihydroxy- compound which can be mentioned here. It is obtained by fusing 4-chlorocarbostyril with caustic potash at 200° (Friedlaender and Weinberg, Ber. 1882, 15, 2683); by boiling a solution of ethyl acetylanthranilate in dry toluene with sodium (Camps, Arch. Pharm. 1899, 237, 690; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 102894 of 1898); by fusing potassium acetylanthranilate with caustic potash at 250° (Bad. Anilin- & Soda-Fab., D. R.-P. 117167 of 1900); by hydrolysing ethyl *o*-aminobenzoylacetate with very dilute hydrochloric acid (Erdmann, Ber. 1899, 32, 3570); or by heating *o*-nitrophenylpropiolic acid with sulphuric acid at 145° (Baeyer and Bloem, *ibid.* 1882, 15, 2151).

Properties.—It crystallises in needles, does not melt even at 320°, can be sublimed, and is insoluble in ordinary solvents, but dissolves in acids or alkalis. By nitrous acid it is converted into the 3-iso*nitroso-* derivative (*quinisatoxime*), orange-yellow prisms, m.p. 208° (decomp.), which, when boiled with hydrochloric acid, yields isatin and hydroxylamine (Baeyer and Homolka, Ber. 1883, 16, 2216).

2:4-Dihydroxy-3:4-dihydroquinoline, obtained by reduction of *o*-nitrophenyl-β-lactic acid with ferrous sulphate (Einhorn, Ber. 1884, 17, 2011; D. R.-P. 28900 of 1884), needles (with 2 mol. H_2O), m.p. 95°–97°, or (anhyd.) 149°, gives *carbostyril* when boiled with acidified water, or fused. Its 6-methoxy- derivative, needles, m.p. 177°, synthesised from the corresponding β-lactic acid, was introduced as an antipyretic (Einhorn, D. R.-P. 55119 of 1890).

Alkyl Derivatives.

All the seven isomeric methylquinolines are known. Those containing the alkyl radicle in the 'benzene' nucleus are usually called toluquinolines, the others methylquinolines. In their general properties the alkyl derivatives resemble quinoline; they are mono- acid bases, form double salts with halogen salts of heavy metals, and with alkyl iodides give quaternary ammonium compounds. The 2- and 4-methylquinolines alone call for detailed mention here.

(i.) **Quinaldine** (*2-Methylquinoline*) occurs in coal-tar quinoline to the extent of about 25 p.c. (Jacobsen and Reimer, Ber. 1883, 16, 1084; Jacobsen, D. R.-P. 23967 of 1882). It is obtained synthetically by warming a mixture of aniline and aldol with concentrated hydrochloric acid (Doebner and Miller, Ber. 1883, 16, 2465); by heating crotonic aldehyde with aniline, nitrobenzene and sulphuric acid (Skraup, *ibid.* 1882, 15, 897), or lactic acid with aniline and zinc chloride (Wallach and Wüsten, *ibid.* 1883, 16, 2007; *cf.* Pictet and Duparc, *ibid.* 1887, 20, 3417), or ethylacetanilide with zinc chloride at 250° (Pictet and Bunzl, *ibid.* 1889, 22, 1848); by warming *o*-aminobenzaldehyde and acetone in aqueous solution with a small quantity of caustic soda (Friedlaender and Göhring, *ibid.* 1883, 16, 1835); by heating acetonylquinoline with concentrated hydrochloric acid at 170° (E. Fischer and Kuzel, *ibid.* 165); or by reducing *o*-nitrobenzylideneacetone with stannous chloride and hydrochloric acid (Drewsen, *ibid.* 1954; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 22138; Eng. Pat. 3541 of 1882), but is best prepared by warming a mixture of 1½ parts of paraldehyde, 1 part of aniline, and 2 parts of strong hydrochloric acid for some hours on a water-bath (Doebner and Miller, *l.c.*; Chem. Fab. auf Aktien. (vorm. E. Schering), D. R.-P. 24317 of 1882; Eng. Pat. 956 of 1883; Actieng. für Anilinfab., D. R.-P. 28217; Eng. Pat. 4207 of 1883).

Properties.—It is a colourless, strongly refractive oil, of slight quinoline-like odour, b.p. 238°–239° under 716 mm. (Doebner and Miller, Ber. 1881, 14, 2814); at 244°–245° under 750 mm. (Hoogewerff and van Dorp, Rec. trav. chim. 1884, 3, 344). The salts, as a rule, are readily soluble, but the *chromate*, yellowish-red needles, is only sparingly soluble in cold water (Doebner and Miller, Ber. 1882, 15, 3075). The *platinichloride* forms prisms, m.p. 228°–229°, and the *picrate*, sparingly soluble needles, m.p. 191° (Pictet and Bunzl, *l.c.*).

Reactions.—(1) By oxidation with concentrated nitric acid, quinaldine is converted into a *nitroquinoline-2-carboxylic acid* (Doebner and Miller, Ber. 1882, 15, 3076); with potassium permanganate it forms *acetylanthranilic acid* and oxalic acid (*ibid.* 3077), and with chromium trioxide and sulphuric acid it yields *quinaldic* (quinoline-2-carboxylic) *acid* (Doebner and Miller, *ibid.* 1883, 16, 2472).

(2) On reduction with tin and hydrochloric acid it gives the *tetrahydro-* derivative (Doebner and Miller, Ber. 1883, 16, 2467).

(3) On nitration, preferably below 4°, excess of nitric acid being avoided, it furnishes a mixture of the 5-*nitro-* and 8-*nitro*-quinaldines, the former being the chief product (Decker and Remfrey, Ber. 1905, 38, 2776; *cf.* Doebner and Miller, *ibid.* 1884, 17, 1699; Gerdeissen, *ibid.* 1889, 22, 245).

(4) When sulphonated with anhydrosulphuric acid at 100°, quinaldine yields a mixture of the 6-, *meta-*,[1] and 8-*monosulphonic acids*, of which the 'meta-' acid constitutes nearly two-thirds and the 8- acid nearly one-third (Doebner and Miller, Ber. 1884, 17, 1703; Chem. Fab. auf Aktien. (vorm. E. Schering), *l.c.*; D. R.-P. 29819 of 1883).

(5) Owing to the reactivity of the 2-methyl group, it yields condensation products with aldehydes, thus resembling 2-methylpyridine (α-picoline). From the product with chloral, α-quinolineacrylic acid and *quinoline*-2-*aldehyde* have been prepared (Miller and Spady, Ber. 1885, 18, 3404; 1886, 19, 130; Einhorn, *ibid.* 1885, 18, 3467; Farb. vorm. Meister, Lucius & Brüning, D. R.-P. 36964 of 1885).

(6) When heated with phthalic anhydride and zinc chloride it is converted into *quinophthalone* (Jacobsen and Reimer, Ber. 1883, 16, 1082; *v.* p. 482).

(ii.) **Lepidine** (4-*Methylquinoline, Iridoline*) occurs in the product formed by distilling cinchonine with caustic potash (Greville Williams, Trans. R. S. Edin. 1856, 21, iii., 377), and is isolated from the fraction, b.p. 250°–260°, by dissolving it in 3–4 parts of warm alcohol, adding 2 parts of sulphuric acid of sp.gr. 1·53, and decomposing the crystalline acid sulphate which separates by potash (Hoogewerff and van Dorp, Rec. trav. chim. 1883, 2, 1). Synthetically it has been prepared by saturating a mixture of methylal and acetone with gaseous hydrogen chloride, and then heating it with aniline and concentrated hydrochloric acid (Beyer, J. pr. Chem. 1886, [2] 33, 418; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 35133 of 1885); also by distilling 2-hydroxylepidine with zinc dust (Knorr, Annalen, 1886, 235, 94); or by heating lepidine-2-carboxylic acid above its fusing-point (Koenigs and Mengel, Ber. 1904, 37, 1324).

Properties.—It is an oil, b.p. 265·5° under 746·7 mm., sp.gr. 1·0862 at 20° (Krakau, *cf.* Chem. Soc. Abstr. 1886, 50, 162), has the odour of quinoline, and is miscible in all proportions with alcohol, ether, benzene, or light petroleum. The *platinichloride* forms triclinic crystals, m.p. 226°–230° (Knorr, *l.c.*), the *picrate*, crystals, m.p. 212°–213° (Krakau, *l.c.*), the *methiodide*, prisms, m.p. 173°–174° (Hoogewerff and van Dorp, *l.c.*).

Reactions.—(1) By chromic acid mixture it is oxidised to *cinchonic* (quinoline-4-carboxylic) *acid*, but with alkaline permanganate it gives *pyridine*-2 : 3 : 4-*tricarboxylic acid* (Hoogewerff and van Dorp, Ber. 1880, 13, 1640).

(2) Like quinaldine, it furnishes condensation products with aldehydes (Koenigs, Ber. 1898, 31, 2364; Loew, *ibid.* 1903, 36, 1166).

(3) For *nitro-* and *amino-* derivatives, *sulphonic acids*, &c., *cf.* Koenigs, Ber. 1890, 23, 2669; Busch and Koenigs, *ibid.* 2679.

The 6-*methoxy-* derivative, m.p. 50°–52° (with 1 mol. H_2O), obtained when quinine is heated with caustic alkali, has been synthesised from *p*-anisidine, acetone and methylal (Pictet and Misner, Ber. 1912, 45, 1801). Like quinine, it gives a green colouration with chlorine water and ammonia (Koenigs, *l.c.*).

The toluquinolines, and many of their derivatives, have been obtained by Skraup's reaction (*cf.* Monatsh. 1885, 6, 761). The 5-, 7-, and 8-toluquinaldines, with hydrogen bromide and bromine, form compounds of the composition $B{\cdot}Br_2{\cdot}HBr$, which, when heated at 150°–200°, are converted into *ω-bromomethylquinolines* $C_{10}H_8N{\cdot}CH_2Br$. The 6- compound behaves differently (Claus, D. R.-P. 98272 of 1897).

2 : 4-Dimethylquinoline, formed by the condensation of acetone and aniline in the presence of nitrobenzene and hydrogen chloride (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 32961 of 1885; *cf.* Beyer, J. pr. Chem. 1886, [2] 33, 401), or of *o*-aminoacetophenone and acetone in caustic alkali solution (O. Fischer, Ber. 1886, 19, 1037), an oil, b.p. 264°–265°, is oxidised by chromic acid to 2-*methylquinoline*-4-*carboxylic acid* (Beyer, *l.c.*), but by permanganate to 2-*methylpyridine*-4 : 5 : 6-*tricarboxylic acid.*

For phenylquinolines, *v.* p. 480.

Quinolinecarboxylic Acids.

Quinolinemonocarboxylic acids, of which all the seven isomerides are known, can be prepared by the following general methods—

(*a*) For those containing the CO_2H group in the 'pyridine' ring: either by oxidation of the corresponding methylquinoline, or by synthetical methods;

(*b*) For those containing it in the 'benzene' ring: either by Skraup's method, or by hydrolysis of the nitrile obtainable from the corresponding amino- derivative by Sandmeyer's method or from the sulphonic acid by distillation with potassium cyanide.

Oxidation of the alkylquinolines is usually effected by means of chromic acid in dilute sulphuric acid, as the action, although slow, is limited to the alkyl groups. With permanganate, the 'benzene' ring is ruptured, leading to the production of pyridinecarboxylic acids, except in the case of 2-alkylquinolines when acyl derivatives of anthranilic acid are obtained.

The quinolinecarboxylic acids are crystalline, readily lose carbon dioxide when heated with lime, and form stable salts both with bases and acids. In many cases they form quaternary ammonium compounds with alkyl iodides, from which betaïnes and not hydroxides result by interaction with silver oxide and water. The only acids which call for detailed mention here are the 2- and the 4- derivatives.

Quinoline-2-carboxylic acid (*Quinaldic acid*), is obtained by oxidation either of quinaldine with chromic acid in dilute sulphuric acid (Doebner and Miller, Ber. 1883, 16, 2472), or of 2-quinolylethanol (formed by the condensation of quinaldine and formaldehyde) with nitric acid of sp.gr. 1·4 (Besthorn and Ibele, *ibid.*

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[1] The evidence that Doebner and Miller's quinaldine-β-sulphonic acid is the 5- and not the 7-derivative rests on Rist's production of a quinaldinecarboxylic acid, m.p. 284°, from '*meta*'-nitroquinaldine (Ber. 1900, 23, 3485; *cf.* Richard, *ibid.* 3490), now known to be the 5- and not the 7- derivative (Decker and Remfry, *supra*).

1906, 39, 2329). The *acid*, HA+$2H_2O$, forms needles, m.p. (anhydrous) 156°; the *chloride*, needles, m.p. 97°–98° (*cf. inter alia*, Besthorn and Ibele, Ber. 1905, 38, 2127; *ibid.* 1906, 39, 2329; Besthorn, *ibid.* 1909, 42, 2697; Meyer and Turnau, *ibid.* 1166). When the acid is heated at 130°–135° with acetic anhydride, or the chloride interacts with quinoline in the cold, a red dye $C_{19}H_{12}ON_2$, m.p. 230°–240°, is obtained (Besthorn and Ibele, Ber. 1904, 37, 1236; 1905, 38, 2127; Besthorn, *ibid.* 1908, 41, 2001; D. R.-P. 168948 of 1905).

Quinoline-4-carboxylic acid (*Cinchonic acid*) is the chief product (50 p.c.) obtained by oxidising cinchonine with chromic acid (Koenigs, Ber. 1879, 12, 97; 1894, 27, 1501); and is formed similarly from cinchonidine, cinchotenine, cinchotenidine (Skraup, Ber. 1879, 12, 230; Annalen, 1880, 201, 303) or lepidine, (Hoogewerff and van Dorp, Rec. trav. chim. 1883, 2, 10). For a synthesis from quinoline methiodide, *cf.* Kaufmann and Peyer, Ber. 1912, 45, 1805. The *acid*, HA+H_2O, forms needles, or HA+$2H_2O$, triclinic or monoclinic prisms, m.p. (anhydrous), 253°–254°; and the *chloride*, needles, m.p. 170° (H. Meyer, Monatsh. 1901, 22, 109). On nitration it yields 5-*nitrocinchonic acid*, from which by reduction the *peri-* anhydride of 5-aminocinchonic acid, m.p. 254°–255°, is obtained (Koenigs and Lossow, Ber. 1899, 32, 717).

Quinic acid (6-*methoxycinchonic acid*), obtained when quinine is oxidised with chromic acid (Skraup, Ber. 1879, 12, 230, 1104), has been synthesised from *p*-anisidine, methylal, and ethyl pyruvate (Pictet and Misner, Ber. 1912, 45, 1801). It forms prisms, m.p. 280°, and in alcoholic, but not aqueous solution, shows blue fluorescence.

TETRAHYDRO- DERIVATIVES.

(i.) **Tetrahydroquinoline** is obtained from quinoline by reduction with zinc and hydrochloric acid (Wyschnegradsky, Ber. 1879, 12, 1481), tin and hydrochloric acid (*ibid.* 1880, 13, 2400; Hoffmann and Koenigs, Ber. 1883, 16, 728), sodium amalgam (Koenigs, *ibid.* 1881, 14, 100), sodium and alcohol (Weidel and Gläser, Monatsh. 1886, 7, 328), or electrolytically in dilute sulphuric acid solution (Ahrens, *cf.* Chem. Soc. Abstr. 1897, 72, i. 369; Merck, D. R.-P. 90308 of 1896; 104664; Eng. Pat. 21471 of 1898). It is also formed from 2-hydroxyquinoline by reduction with sodium and alcohol (Knorr and Klotz, Ber. 1886, 19, 3302). To isolate the base, the reduction product, if acid, is made alkaline and distilled with steam; tetrahydroquinoline and unchanged quinoline pass over, and the former is precipitated as hydrochloride by passing hydrogen chloride into a dry ethereal extract of the distillate (Hoffmann and Koenigs, *l.c.*).

Properties.—It is an oil, which solidifies in a freezing mixture, b.p. 251° (corr.), sp.gr. 1·0627 at 15°/15° (Perkin, Chem. Soc. Trans. 1896, 69, 1214), and has the properties of a secondary alkylated aniline (*cf.* Bamberger and Wulz, Ber. 1891, 24, 2055). It is oxidised to quinoline by nitrobenzene (Lellmann and Reusch, Ber. 1889, 22, 2390), mercuric oxide (Tafel, *ibid.* 1892, 25, 1622), silver nitrate (*ibid.* 1894, 27, 824), or iodine (Schmidt, Arch. Pharm. 1899, 237, 561). The 'piperidine' ring of its quaternary ammonium derivatives is not ruptured by the Hofmann method, but by reduction with sodium amalgam and water (Emde, Annalen, 1912, 391, 90). Its *benzoyl* derivative, m.p. 75°, on oxidation by permanganate yields *benzoylisatic acid* (Hoffmann and Koenigs, *l.c.*). The *hydrochloride* forms needles, m.p. 180° (Friedlaender and Ostermaier, Ber. 1882, 15, 335).

1-Methyltetrahydroquinoline, obtained either by methylation of tetrahydroquinoline (Hoffmann and Koenigs, Ber. 1883, 16, 732), or by reduction of tetrahydroquinoline methiodide with tin and hydrochloric acid (Feer and Koenigs, *ibid.* 1885, 18, 2388), or, mixed with 2-methylquinolone, by the action of caustic alkali solution on quinoline methiodide (Decker, Ber. 1903, 36, 2568), is an oil, b.p. 242°–244° under 720 mm., sp.gr. 1·022 at 20°/4°, which resembles dimethylaniline in many of its properties. The *sulphate*, **Kairoline,** was at one time used as an antipyretic; the *picrate* forms yellow needles, m.p. 144·5° (Decker, *l.c.*).

2-Methyltetrahydroquinoline (*tetrahydroquinaldine*), obtained by reducing quinaldine by tin and hydrochloric acid (Doebner and Miller, Ber. 1883, 16, 2467), is an oil, b.p. 250° corr., sp.gr. 1·042 at 16°/4° (Ladenburg, *ibid.* 1894, 27, 77). The base has been resolved into its optical antipodes (Pope and Peachey, Chem. Soc. Trans. 1899, 75, 1066; Pope and Read, *ibid.* 1910, 97, 2199).

(ii.) 6-**Hydroxytetrahydroquinoline,** formed by reducing 6-hydroxyquinoline with tin and hydrochloric acid, is crystalline, m.p. 148°; its *acetyl* derivative crystallises in needles, m.p. 82° (Bad. Anilin- & Soda-Fab., D. R.-P. 42871 of 1887).

Its methyl ether, **thalline,** $C_9H_{10}N{\cdot}OCH_3$, formed when 6-methoxyquinoline is reduced by tin and hydrochloric acid (Bad. Anilin- & Soda-Fab., D. R.-P. 30426 of 1884; Skraup, Monatsh. 1885, 6, 767), or 6-hydroxytetrahydroquinoline is methylated by any of the ordinary processes (Bad. Anilin- & Soda-Fab., D. R.-P. 42871 of 1887), forms rhombic prisms, m.p. 42°–43°, b.p. 283° under 735 mm., and dissolves only very sparingly in cold water, but readily in alcohol. The aqueous solutions of its salts are coloured an intense green by ferric chloride, chlorine water, or other oxidising agents. Of these salts, the *sulphate*, $B_2{\cdot}H_2SO_4+2H_2O$, needles, soluble in 5 pts. of water at the ordinary temperature; and the *tartrate*, $B{\cdot}C_4H_6O_6$, prisms, soluble in 10 pts. of water at 15°, were at one time employed as antipyretics.

(iii.) 8-**Hydroxytetrahydroquinoline,** obtained by reduction of 8-hydroxyquinoline with tin and hydrochloric acid, crystallises in needles, m.p. 121°–122°, is not volatile with steam, and dissolves fairly readily in hot water (Bedall and O. Fischer, Ber. 1881, 14, 1368). Both this base and its 1-alkyl derivatives can be used as photographic developers (Lembach and Schleicher, D. R.-P. 86978, 89181 of 1895).

The 1-methyl derivative, $OH{\cdot}C_9H_9N{\cdot}CH_3$, **Kairine,** prepared by mixing carefully the tetrahydro- base with methyl iodide, and completing the reaction in a reflux apparatus (O. Fischer, Ber. 1883, 16, 714; D. R.-P. 21150; Eng. Pat. 3044 of 1882), crystallises from alcohol in prisms, m.p. 114°, dissolves only sparingly in water, but readily in warm alcohol, and in alcoholic solution gives with ferric chloride a deep brown colouration. The readily soluble *hydrochloride*, B·HCl+H_2O, was at one time employed as a febrifuge.

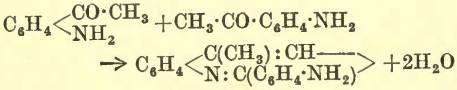
The 1-ethyl derivative, which closely resembles the 1-methyl compound, forms monoclinic prisms, m.p. 76° (O. Fischer, Ber. 1883, 16, 717; O. Fischer and Renouf, *ibid.* 1884, 17, 756). Similarly, its *hydrochloride*, B·HCl (Kairine A), has antipyretic properties.

PHENYLQUINOLINES.

Both in their mode of preparation and in many of their properties, the phenylquinolines show much resemblance to the alkylquinolines. Those containing the aryl group in the 2- or 3-position can be prepared by reactions similar to those employed by Doebner and Miller, or by Friedlaender for alkylquinolines (*cf.* Doebner and Miller, Ber. 1883, 16, 1665; Friedlaender and Göhring, *ibid.* 1835; *v.* pp. 472, 473), and those containing it in the 6- or 8- position by Skraup's reaction (*cf.* La Coste and Sorger, Annalen, 1885, 230, 8). As radicles such as Cl, NO_2, NH_2, SO_3H, OH, and CO_2H may occur in the aryl group, in addition to substituents present in the quinoline complex, the number of phenylquinoline derivatives is large. Reference can be made here only to those which furnish dyestuffs or are related to cinchona alkaloids.

2-Phenyl-4-methylquinoline (*flavoline*), obtained by heating flavenol with zinc dust (O. Fischer and Rudolph, Ber. 1882, 15, 1503), or *o*-aminoacetophenone with a solution of acetophenone in aqueous alcohol rendered alkaline with caustic soda (O. Fischer, *ibid.* 1886, 19, 1037), forms prisms, m.p. 64°–65°, b.p. 373°–375° (Bernthsen and Hess, *ibid.* 1885, 18, 34). It is scarcely attacked by chromic acid mixture, but readily oxidised by alkaline permanganate. On nitration with fuming nitric acid at 50°–60°, it gives the 4′-*nitro*- derivative, which has an odour of musk, and when reduced yields *flavaniline* (Besthorn and O. Fischer, Ber. 1883, 16, 68).

Flavaniline (4′-*amino*-2-*phenyl*-4-*methylquinoline*) was first prepared by heating acetanilide with zinc chloride at 250°–270° (O. Fischer and Rudolph, Ber. 1892, 15, 1500; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 19766; Eng. Pat. 5427 of 1881), its constitution being ascertained partly by its conversion into flavenol by the diazo- reaction (O. Fischer and Rudolph, *l.c.*) and partly by its synthesis from a mixture of *o*-amino- and *p*-amino-acetophenone with zinc chloride at 100°



$$C_6H_4{<}\begin{matrix}CO\cdot CH_3\\NH_2\end{matrix} + CH_3\cdot CO\cdot C_6H_4\cdot NH_2 \rightarrow C_6H_4{<}\begin{matrix}C(CH_3):CH\text{——}\\N:C(C_6H_4\cdot NH_2)\end{matrix}{>} + 2H_2O$$

(O. Fischer, Ber. 1886, 19, 1038).

It can also be obtained by heating aniline hydrochloride with acetic anhydride at 180°–200° (Baum, D. R.-P. 27948 of 1883), or acetanilide hydrochloride at 280° (Noelting and Weingärtner, Ber. 1885, 18, 1341), or acetyl-*o*-aminobenzoic acid with dehydrating agents (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 21682; Eng. Pat. 1724 of 1882), or acetophenoneoxime with phosphoric oxide at 60° (Goldschmidt, Chem. Zeit. 1903, 27, 279).

Properties.—It crystallises from benzene in prisms, m.p. 97°, volatilises without decomposition, and dissolves only very sparingly in water, but readily in alcohol. It forms two series of salts, those with 1 mol. of a monobasic acid being yellowish-red, but those with 2 mols. colourless. The *hydrochloride* $C_{16}H_{14}N_2$,HCl has been employed as a bright-yellow dye for silk and wool (Köchlin, Dingl. poly. J. 1884, 253, 86). It dissolves in sulphuric acid, but is sulphonated by anhydrosulphuric acid, forming Flavaniline-S., a greenish-yellow dye for wool.

*iso*Flavaniline (2′-*amino*-2-*phenyl*-4-*methylquinoline*), giving an intense yellow solution in cold water or alcohol (Bischler and Burkart, Ber. 1893, 26, 1353), and 6-*amino*-4-*phenylquinoline* (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 79385 of 1895) have been described.

Flavenol (4′-*hydroxy*-2-*phenyl*-4-*methylquinoline*), obtained from flavaniline by the diazo-reaction, forms scales, m.p. 238°, dissolves only sparingly in alcohol, but readily in caustic soda solution, and is insoluble in ammonia. On distillation with zinc dust it yields *flavoline*, and on oxidation with alkaline permanganate it yields as final product *pyridine*-2:4:5:6-*tetracarboxylic acid* (O. Fischer and Täuber, Ber. 1884, 17, 2926).

Among the hydroxy-4-phenylquinolines are two degradation products of cinchonine and cinchonidine, viz. *apo*cinchenine (*apo*cinchine), and *apo*quinenine (*apo*chinine), *cf.* Koenigs, Ber. 1893, 26, 713; 1894, 27, 901. Also, of the three isomeric 4-phenolquinolines which have been synthesised, 2′-*hydroxy*-4-*phenylquinoline* is a degradation product of *apo*cinchenine (Koenigs and Nef, Ber. 1887, 20, 622; Besthorn and Jaeglé, *ibid.* 1894, 27, 907; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 79173 of 1894).

Descriptions of the preparation of the following aryl derivatives are to be found in the Patent literature: 2′-, 3′- and 4′-*hydroxy*-4-*phenylquinaldine* (Farbw. vorm. Meister, Lucius & Brüning. D. R.-P. 80501 of 1894); 6-*hydroxy*-4-*phenylquinaldine* (*ibid.* D. R.-P. 79871 of 1894); 6-*methoxy*-4-*phenylquinaldine* (*ibid.* D. R.-P. 35133 of 1885).

QUATERNARY AMMONIUM COMPOUNDS.

Quaternary ammonium (quinolinium) compounds are obtained by the combination of quinoline, its homologues, and the greater number of its derivatives, with alkyl iodides. Reference to two only of these compounds can be made here.

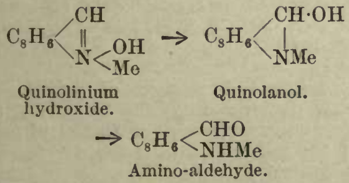
Quinoline methiodide, obtained from a solution of dry quinoline and methyl iodide in benzene either kept in the cold (Kaufmann and Albertini, Ber. 1909, 42, 3779), or heated in an efficient reflux apparatus (Marckwald and Meyer, *ibid.* 1900, 33, 1884; Decker, *ibid.* 2276), forms yellow crystals, m.p. 133°, which separate from dilute alcohol as the hydrate $C_{10}H_{10}NI+H_2O$, m.p. 72° (Decker, Ber. 1903, 36, 1205, 2568).

Quinoline ethiodide, forms yellow needles, m.p. 158°–160° (Hoogewerff and van

Dorp, Rec. trav. chim. 1883, 2, 321), and when heated at 280°–290° is converted into a mixture of 2- and 4-*ethylquinoline* with diethylquinoline (Reher, Ber. 1886, 19, 2996).

From the quinolinium alkyl iodides three types of compound can be obtained by interaction with caustic alkali. These are the quinolones, the *apo*cyanines, and the cyanines, the last-named being dye-stuffs which—although too fugitive for ordinary dyeing purposes—are valuable as sensitisers in photographic work. The conditions under which they are formed are given in the following sections: I (quinolines), II (*apo*cyanines and cyanines).

I. When quinolinium alkyl iodides interact with a solution of caustic alkali or a suspension of silver oxide in water, bases are precipitated, as a rule,[1] which differ from the expected quaternary ammonium hydroxides[2] by being insoluble in ether, but are reconverted into the quinolinium salts by combination with acids (*cf.* Claus and Himmelmann, Ber. 1880, 13, 2045). In alkaline solution these bases, like aldehydes, suffer both oxidation and reduction, giving a mixture of quinolone and tetrahydroquinoline, and they are oxidised by alkaline ferricyanide solution forming *quinolones* (Decker, Ber. 1891, 24, 690; 1892, 25, 443, 3326; 1903, 36, 2568). When boiled with alcohol they form mixed ethers ('alcoholates'), and they give anhydrides ('oxides') when heated with benzene (La Coste, Ber. 1882, 15, 189; Hantzsch and Kalb, *ibid.* 1899, 32, 3119; Kaufmann and Strübin, *ibid.* 1911, 44, 682). Decker considers them to be quinolanols (Ber. 1892, 25, 3326), but, while intermediate compounds of this type may occur in the reaction, the probabilities point to the bases themselves being amino-aldehydes.[3]


Quinolinium hydroxide.

Quinolanol.

Amino-aldehyde.

(Roser, Annalen, 1892, 272, 221; 1894, 282, 393; Gadamer, Arch. Pharm. 1905, 243, 12; 1908, 246, 89; Kaufmann and Strübin, *l.c.*; Kaufmann and Plá y Janini, Ber. 1911, 44, 2670).

II. By the substitution of methyl alcohol as solvent for the alkali in place of water, the end product of the reaction becomes an *apo*cyanine or a cyanine, according as the quinolinium alkyl iodide employed is a single substance or a mixture containing quinaldine or lepidine derivatives.

***apo*Cyanines.** The *apo*cyanines are formed when for each molecule of the quinolinium alkyl iodide, ½–⅔ molecule of caustic alkali is used, two products being obtained, viz. the yellow *xanthocyanines* and the red *erythrocyanines.* A typical preparation is the following: To a solution of quinolinium methyl iodide (28·5 grms) in boiling methyl alcohol (15 c.c.), two additions (each 14 c.c.) of 10 p.c. methyl-alcoholic potash are made, with an interval of ten minutes between them, and the product left to crystallise. From the crystalline separation, extraction with methyl alcohol removes the erythrocyanine, leaving a yellow residue of the less soluble xanthocyanine (Kaufmann and Strübin, Ber. 1911, 44, 694; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 154448 of 1903).

These dyes are distinguished from the cyanines by the fact that in aqueous solution they are not decolourised at once by acids; alkalis also do not affect the colour of their solutions. For their constitution, *cf.* Kaufmann and Strübin, *l.c.*; Decker and Kaufmann, J. pr. Chem. 1911, [2] 84, 239.

Cyanines. The first cyanine or quinoline-blue was prepared by Greville Williams, who obtained it by the action of caustic alkali on the product formed by heating quinoline (from cinchonine, but not from coal-tar) with amyl iodide (Trans. R. S. Edin. 1856, 21, 377; Chem. News, 1863, 2, 219). Hofmann showed it to be a derivative of quinoline and lepidine (Roy. Soc. Proc. 1863, 12, 410), and Hoogewerff and van Dorp gave to dyes of this class the formula $C_{19}H_{13}N_2,XYI$ (in which X and Y are alkyl groups), representing the cyanine reaction thus:

$$C_9H_7N{\cdot}XI+C_{10}H_9N{\cdot}YI+KOH$$
$$=C_{19}H_{13}N_2{\cdot}XYI+KI+H_2O+H_2.$$

They also found that while blue dyes result from the condensation with lepidine, reddish-violet *iso*cyanines are formed with quinaldine (Rec. trav. chim. 1883, 2, 28; 1884, 3, 317; *cf.* Spalteholz, Ber. 1883, 16, 1847).

Preparation.—Various modifications of the original method of preparation or mode of purification have been proposed (*cf.* Hoogewerff and van Dorp, *l.c.*), but in none of these is account taken of the simultaneous production of *apo*cyanines. Kaufmann and Vonderwahl obtain ethyl-red by the interaction of quinolinium ethiodide (2 mols.), quinaldinium ethiodide (1 mol.), and caustic potash (1 mol.) in cold alcohol (1 litre for 50 grams of the mixed iodides). After two days, the crystalline separation is removed, and a further separation obtained by concentration of the mother liquor. These separations, a mixture of ethyl-red with diethylerythro*apo*cyanine, are purified by crystallisation from alcohol in which ethyl-red is only sparingly soluble. The yield of *apo*cyanine is about double that of the ethyl-red, but it diminishes with a corresponding increase in that of the *iso*cyanine if the operation is conducted in boiling alcohol (Ber. 1911, 44, 1409; *cf.* Miethe and Traube, D. R.-P. 142926 of 1902).

Properties.—The cyanines crystallise well, usually with water or alcohol of crystallisation, and have an intense colour, but are at once decolourised by acids. They are the mono-acid salts of diacid bases, the normal or di-acid salts being colourless or yellow, and readily decomposed into the dye (mono- acid salt) and acid. They form sparingly soluble *periodides*, from which the cyanine can be recovered by interaction with alkali. On silk they give very beautiful blue shades, but being fast neither to light nor acids are valueless as dyes.

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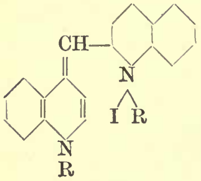
[1] The degree of readiness with which this reaction takes place is greatly influenced by substituents, such as NO_2, NH_2, etc., present in the molecule (*cf.* Decker and Kaufmann, J. pr. Chem. 1911, [2] 84, 441).

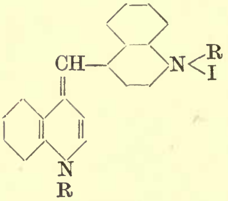
[2] In solutions of *iso*quinoline but not of quinoline derivatives, an equilibrium is set up between the ammonium hydroxide and the base (Decker and Kaufmann, J. pr. Chem. 1911, [2] 84, 225, 425), and the production of 'phenolbetaïnes' from hydroxyquinoline alkyl iodides also affords evidence that the ammonium hydroxides are formed in the first instance.

[3] For the rupture of the 'pyridine' ring and formation of an aldehyde, which this view entails, an analogous case exists in Reissert's observation that quinoline in the presence of benzoyl chloride and caustic soda is converted into *o*-benzoylaminocinnamic aldehyde (Ber. 1905, 38, 3415).

Constitution.—For the production of *iso*cyanines, quinaldine is essential: *iso*cyanines can be obtained from quinaldinium alkyl iodides in the absence of other quaternary iodides, but not from lepidinium alkyl iodides under this condition (Hoogewerff and van Dorp, *l.c.*; *cf.* Miethe and Book, Ber. 1904, 37, 2008, 2821). From a consideration of the investigations of Hoogewerff and van Dorp (*l.c.*), Decker (Ber. 1891, 24, 692), Vongerichten and Höfchen (*ibid.* 1908, 41, 3054), Miethe and Book (*ibid.* 1904, 37, 2008, 2821), and Kaufmann and Strübin (*l.c.*), and of the results of their own work, Kaufmann and Vonderwahl draw the conclusion that the formulæ proposed by Koenig (J. pr. Chem. 1906, [2] 73, 100) afford the best representation of the structure of these dyes (R being the alkyl group)—



*iso*Cyanine.



Cyanine.

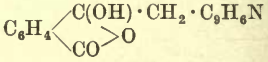
(Ber. 1912, 45, 1407; *cf.* Decker and Kaufmann, J. pr. Chem. 1911, 84, [2] 235).

Use as sensitisers in photography (*cf.* Sheppard, Chem. Soc. Trans. 1909, 95, 15). The cyanines have the valuable property of sensitising the photographic plate for yellow and red light. Those from lepidine sensitise to the C line, but those from quinaldine are effective only so far as D½C (*cf.* Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 167139 of 1903). By increasing the molecular weight of *iso*cyanines the range can be extended; for example, 'Orthochrom-T,' obtained from 6-toluquinaldine ethiodide mixed with 6-toluquinoline ethiodide, sensitises to the C- line, and by modifications of this device *iso*cyanines can be produced which have the advantages over cyanines that they cause no fogging, do not diminish the total sensitiveness of the plate, and give a continuous sensitising band, unbroken in the green (Farbw. vorm. Meister, Lucius & Bruning, D. R.-P. 167159, 167770; Eng. Pat. 9598 of 1903). By the use of β-naphthaquinaldine ethiodide with quinoline ethiodide, sensitising as far as the B-line is achieved (Aktieng. für Anilinfab., D. R.-P. 158349; Eng. Pat. 9456 of 1904).

Instead of alkyl iodides dialkyl sulphates have been used with satisfactory results for the production of quinolinium compounds in the manufacture of cyanines (Farbenfab. vorm. F. Bayer & Co., D. R.-P. 158078, 170048, 170049; Eng. Pat. 25144 of 1903). The interaction of the alkyl iodides or dialkyl sulphates of the quinoline and quinaldine bases with caustic potash, or better with an alkali sulphite, can be carried out in hot aqueous, alcoholic, or pyridine solution in the presence of formaldehyde (methylal), of sodium glyoxylate followed by an oxidising agent, or of chloroform, bromoform or iodoform, greenish-blue or bluish-green 'pinacyanol' dyes being produced which are said to be the best pansensitisers known (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 172118; Eng. Pat. 16227 of 1905; D. R.-P. 175034, 178688 of 1906; 189942, 200207 of 1907).

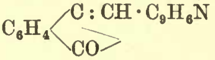
QUINOLINE-YELLOW.

From quinaldine by condensation with phthalic anhydride in the presence of zinc chloride three products can be obtained, according to the temperature employed. These have the structural formulæ:—



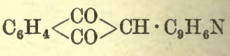
$$C_6H_4{<}\begin{matrix}C(OH)\cdot CH_2\cdot C_9H_6N\\ CO\end{matrix}{>}O$$

I (at 120°).



$$C_6H_4{<}\begin{matrix}C:CH\cdot C_9H_6N\\ CO\end{matrix}$$

II (at 160°).



$$C_6H_4{<}\begin{matrix}CO\\ CO\end{matrix}{>}CH\cdot C_9H_6N$$

III (at 200°).

and the final product III, symmetrical quinophthalone, is the parent substance of the dyestuff quinoline-yellow.

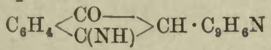
Quinophthalone (sym.-*quinophthalone*; 2-*quinolylindandione*; formula III) can be prepared by heating quinaldine and phthalic anhydride in mol. prop. with zinc chloride at 200° (Jacobsen and Reimer, Ber. 1883, 16, 1082, 2602; *cf.* Traube, *ibid.* 298); or, quantitatively, by heating quinaldine with ethyl phthalate and sodium at 100° (Eibner and Lange, Annalen, 1901, 335, 346); *or* by heating *iso*quinophthalone (formula II) at 240°–250° with sodium ethoxide or benzaldehyde (Eibner and Merkel, Ber. 1902, 35, 2298); *or* by warming the compound I with caustic soda solution (Eibner and Lange, *l.c.*).

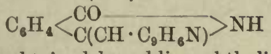
Preparation.—A mixture of quinaldine (5 pts.) and phthalic anhydride (6 pts.) is fused with zinc chloride (6 pts.) at 200°–210° for 5–6 hours; the melt boiled with dilute hydrochloric acid to extract zinc chloride, phthalic acid and unattacked base; and the insoluble residue filtered, ground, and dried (Jacobsen and Reimer, D. R.-P. 23188 of 1882; 25144; Eng. Pat. 1362 of 1883). The product contains *iso*quinophthalone in amount which, depending on the temperature employed, may reach 25 p.c., but this can be transformed into quinophthalone by heating the melt with alcoholic sodium ethoxide until a uniform red mass is obtained. After filtration, the residue is boiled with water to decompose the sodium salt and then dried (Eibner and Merkel, Ber. 1902, 35, 2298; 1904, 37, 3008; Eibner, D. R.-P. 158761 of 1903).

Properties.—Quinophthalone crystallises in golden-yellow needles, m.p. 240°, is insoluble in water, sparingly soluble in boiling alcohol, but readily soluble in acetic acid and chloroform. With sodium and potassium ethoxides it gives the *sodium* and *potassium* salts, which form orange-red needles, and with water regenerate the quinophthalone (Eibner and Merkel, Ber. 1904, 37, 3007).

Reactions.—(1) When heated with hydrochloric acid at 240°, or fused with caustic alkali, it is resolved into *quinaldine* and *phthalic acid.*

(2) When heated with alcoholic ammonia at 200° for 40 hours it is converted into *α-quinophthalin,* a basic yellow colouring matter (Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 27785 of 1883), forming garnet-red leaflets, m.p. 305° (Eibner and Hofmann, Ber. 1904, 37, 3021), isomeric with *β-quinophthalin,* pale yellow prisms,

(α) 
$$C_6H_4\left<\begin{matrix}CO\text{———}\\C(NH)\end{matrix}\right>CH\cdot C_9H_6N$$

(β) 
$$C_6H_4\left<\begin{matrix}CO\text{—————}\\C(CH\cdot C_9H_6N)\end{matrix}\right>NH$$

m.p. 213°, obtained by adding phthalimide to a mixture of quinaldine and zinc chloride at 160°–180° (Eibner and Lange, *l.c.*; Eibner and Hofmann, *l.c.*).

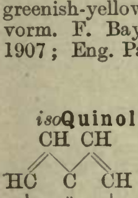
(3) It dissolves in sulphuric acid, but is sulphonated by anhydrosulphuric acid in the cold, forming **quinoline-yellow,** which consists of a mixture of quinophthalonemono- and disulphonic acids; the sodium salt, obtained from this product, is a soluble yellow powder, which dyes wool a fast greenish-yellow in an acid bath.

*iso***Quinophthalone** (unsym-*quinophthalone,* 2-*quinaldylene-phthalide;* Formula II), formed when the quinophthalone reaction (p. 482) is carried out at a temperature not exceeding 160°, crystallises in orange-yellow prisms, m.p. 186°, dissolves only sparingly in alcohol but easily in chloroform, and when heated at 240°–250°, or with benzaldehyde, or with sodium ethoxide, is converted into *quinophthalone.* On digestion with alcoholic ammonia at 100°, it furnishes *quinaldine* and *phthalamide;* and with anhydrosulphuric acid at 100°, it forms quinoline-yellow (Eibner and Merkel, Ber. 1902, 35, 2297; *cf.* 1904, 37, 3008).

Homologues of both *sym-* and *unsym-*quinophthalone have been prepared, and these increase in intensity, fastness to light, covering power, and insolubility in alcohol with increase in molecular weight (Eibner and Hofmann, Ber. 1904, 37, 3017; Eibner, D. R.-P. 158761 of 1903).

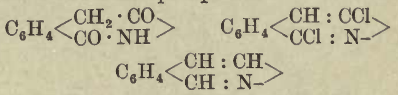
By the substitution of β-thiophthalic acid for phthalic anhydride in these condensations, compounds are obtained which dye unmordanted cotton in yellow shades, and on oxidation by the air or with dichromate give very fast colours (Gesellsch. chem. Ind. Basel, D. R.-P. 189943 of 1906; Eng. Pat. 4159 of 1907). The condensation product from 6-chloroquinaldine and phthalic anhydride on sulphonation furnishes a greenish-yellow dye for silk or wool (Farbenfab. vorm. F. Bayer & Co., D. R.-P. 204255 of 1907; Eng. Pat. 28266 of 1908).

*iso***Quinoline.** This base is a constituent of coal-tar quinoline, and can be isolated from this source by taking advantage of the fact that the acid sulphates of quinoline and quinaldine are more soluble in alcohol than the *iso*quinoline salt. The crystalline sulphate, which separates from an alcoholic solution of the acid sulphates of coal-tar quinoline, is decomposed by caustic potash, and the fraction, b.p. 236°–243°, reconverted into acid sulphate, is repeatedly crystallised from twice its weight of 88 p.c. alcohol until the m.p. rises to 205° (Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 125, 285; 1886, 5, 305; *cf.* Dewar, Roy. Soc. Proc. 1880, 30, 167).



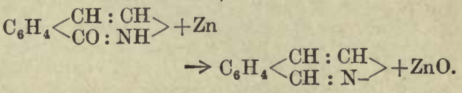
Syntheses.—The methods devised for the synthesis of *iso*quinoline and its derivatives are less general in their scope than those employed in the quinoline series. The following are perhaps the most important of these methods, as they serve both to throw light on the constitution of *iso*quinoline, and to illustrate the connection between this base and the alkaloids.

(1) The first synthesis of *iso*quinoline was effected by heating homophthalimide with phosphorus pentachloride, the dichloro*iso*quinoline thus formed being then reduced by hydriodic acid and phosphorus—

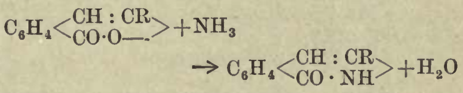

$$C_6H_4\left<\begin{matrix}CH_2\cdot CO\\CO\cdot NH\end{matrix}\right> \qquad C_6H_4\left<\begin{matrix}CH:CCl\\CCl:N\text{—}\end{matrix}\right>$$
$$C_6H_4\left<\begin{matrix}CH:CH\\CH:N\text{—}\end{matrix}\right>$$

(Gabriel, Ber. 1886, 19, 1655, 2361).

(2) *iso*Quinoline has been obtained by heating with zinc dust, homophthalimide (Le Blanc, Ber. 1888, 21, 2299); *iso*carbostyril (Bamberger and Kitschelt, *ibid.* 1892, 25, 1147); or *iso*carbostyrilcarboxylic acid (Zincke, *ibid.* 1497; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 65947 of 1892)

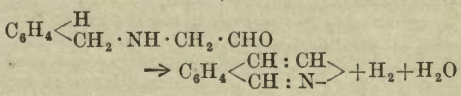

$$C_6H_4\left<\begin{matrix}CH:CH\\CO:NH\end{matrix}\right>+Zn \rightarrow C_6H_4\left<\begin{matrix}CH:CH\\CH:N\text{—}\end{matrix}\right>+ZnO.$$

*iso*Carbostyril and certain of its derivatives can be synthesised from *iso*cumarin and its derivatives by condensation with ammonia, methylamine or aniline in cold aqueous or warm alcoholic solution


$$C_6H_4\left<\begin{matrix}CH:CR\\CO\cdot O\text{—}\end{matrix}\right>+NH_3 \rightarrow C_6H_4\left<\begin{matrix}CH:CR\\CO\cdot NH\end{matrix}\right>+H_2O$$

(Bamberger and Kitschelt, *l.c.*; Zincke, *l.c.*; Bamberger and Frew, Ber. 1894, 27, 198); or they may be obtained from diacyl derivatives of *o*-cyanobenzyl cyanide (homophthalimide) by warming these with alkalis and boiling the resulting cyano*iso*carbostyrils with sulphuric acid (Gabriel and Neumann, Ber. 1892, 25, 3563; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 69138 of 1892; Damerow, Ber. 1894, 27, 2322).

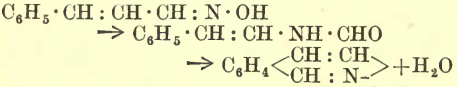
(3) It is formed by dissolving benzylaminoacetaldehyde in anhydrosulphuric acid (E. Fischer, Ber. 1893, 26, 764), or by heating benzylideneaminoacetal with sulphuric acid at 150°–170° (Pomeranz, Monatsh. 1893, 14, 118; Farbw. vorm. Meister, Lucius & Brüning, D. R.-P. 80044 of 1894).


$$C_6H_4\left<\begin{matrix}H\\CH_2\cdot NH\cdot CH_2\cdot CHO\end{matrix}\right. \rightarrow C_6H_4\left<\begin{matrix}CH:CH\\CH:N\text{—}\end{matrix}\right>+H_2+H_2O$$

Derivatives of *iso*quinoline are obtained by condensing aminoacetal in sulphuric acid solution with acetophenone (Pomeranz, Monatsh.

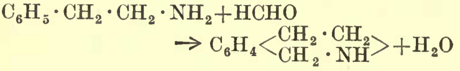
1894, 15, 304), alkylated *m*-hydroxybenzaldehydes, or piperonaldehyde (Fritsch, Annalen, 1895, 286, 1; D. R.-P. 85556; 86561; D. P. Anm. F. 7830 of 1894).

(4) It can be prepared by the interaction of phosphoric oxide and cinnamaldoxime (Bamberger and Goldschmidt, Ber. 1894, 27, 1955, 2795) or benzylidene-acetone (Goldschmidt, *ibid.* 1895, 28, 818). Probably the reaction is dependent on the formation of acyl derivatives of phenylethylamine by the Beckmann change



$$C_6H_5\cdot CH:CH\cdot CH:N\cdot OH \rightarrow C_6H_5\cdot CH:CH\cdot NH\cdot CHO \rightarrow C_6H_4{<}\begin{matrix}CH:CH\\ CH:N-\end{matrix}{>}+H_2O$$

(*cf.* Goldschmidt, Chem. Zeit. 1903, 27, 279) as phenylethylamine and its derivatives, phenylalanine and tyrosine, condense with formaldehyde (methylal in acid solution) furnishing tetrahydro*iso*quinolines



$$C_6H_5\cdot CH_2\cdot CH_2\cdot NH_2+HCHO \rightarrow C_6H_4{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot NH\end{matrix}{>}+H_2O$$

(Pictet and Spengler, Ber. 1911, 44, 2030).

(5) Derivatives of 3 : 4-dihydro*iso*quinoline are produced by heating acyl derivatives of ω-phenylethylamine with zinc chloride or phosphoric oxide (Bischler and Napieralski, Ber. 1893, 26, 1903), or by boiling their solutions in benzene, toluene, or xylene with phosphoric oxide (Pictet and Kay, *ibid.* 1909, 42, 1973), or by condensing the imino- chlorides (prepared from the acyl derivatives by interaction with phosphoric chloride) by the aid of aluminium chloride (Decker and Kropp, *ibid.* 1909, 42, 2075). By oxidation with permanganate in acid solution, these dihydro- compounds are converted into the *iso*quinoline derivatives (Pictet and Kay, *l.c.*).

This reaction, it may be noted, has been applied to the synthesis of the alkaloids, laudanosine (Pictet and Finkelstein, Ber. 1909, 42, 1979), cotarnine (Salway, Chem. Soc. Trans. 1910, 97, 1208), and papaverine (Pictet and Gams, Ber. 1909, 42, 2943).

Preparation.—Benzylideneaminoacetal (1 pt.), obtained in good yield by mixing benzaldehyde and aminoacetal in mol. prop., is added carefully with constant cooling to sulphuric acid (2 pts.), and the solution allowed to mix slowly with sulphuric acid (3 pts.) maintained at 160°–170°. The product, diluted with water, is freed from benzaldehyde by steam, then rendered alkaline and *iso*quinoline removed by distillation with steam. The yield of pure base amounts to about 50 p.c. of that calculated.

Constitution.—When *iso*quinoline is oxidised by potassium permanganate in alkaline solution, it yields both *phthalic acid* and *cinchomeronic* (pyridine-3 : 4-dicarboxylic) *acid* (Hoogewerff and van Dorp, Rec. trav. chim. 1885, 4, 285), but in neutral solution it furnishes *phthalimide* (Goldschmiedt, Monatsh. 1888, 9, 676). From these results, coupled with those obtained by synthetical processes, the formula at the head of this section has been deduced for the base. The positions in the *iso*quinoline formula are numbered from 1 to 8, the nitrogen atom occupying the 2-position.

Properties. — *iso*Quinoline crystallises in tables, m.p. 24·6°, b.p. 240·5° under 763 mm. (Hoogewerff and van Dorp), sp.gr. 1·0986 at 20°/4°, has a quinoline-like odour, and is volatile with steam. It absorbs carbon dioxide from the air, and forms with acids a series of salts, the melting-points of which are higher than those of the corresponding quinoline compounds. The *chromate*, $B_2\cdot H_2Cr_2O_7$, forms needles, decomp. at 150°, the *picrate*, needles, m.p. 222°–223·5° (Pictet and Popovici, Ber. 1894, 25, 734); the *platinichloride*, $B_2\cdot H_2PtCl_6+2H_2O$, needles, m.p. 263° (*ibid.*); the *methiodide*, $B\cdot CH_3I+H_2O$, yellow needles, m.p. 159° (Hoogewerff and van Dorp, *l.c.*). Unlike quinoline it does not give compounds with metallic salts. The *dibromide*, $B\cdot Br_2$, m.p. 82°, yields at 180°–200° a *bromo*iso*quinoline*, m.p. 40° (Edinger and Bossung, J. pr. Chem. 1891, [2] 43, 191); the *tetraiodide* forms dark blue crystals, m.p. 130° (Edinger, *ibid.* 1895, [2] 51, 205).

Reactions.—(1) On reduction with tin and hydrochloric acid, or with sodium and boiling alcohol, it gives *tetrahydro*iso*quinoline* (Bamberger and Dieckmann, Ber. 1893, 26, 1209).

(2) By nitration with concentrated nitric acid it yields the 5- (or 8-) *nitro*iso*quinoline*, m.p. 110°, and, by further nitration, a *dinitro*-derivative (Fortner, Monatsh. 1893, 14, 146; Claus and Hoffmann, J. pr. Chem. 1893, [2] 47, 253).

(3) On sulphonation with 50–60 p.c. anhydrosulphuric acid, it gives a mixture of two *sulphonic acids*, which at 115° contains chiefly the α- (5- or 8- acid), and at 250°–260° chiefly the β- (probably the 6- or 7-) acid (Claus and Raps, J. pr. Chem. 1892, [2] 45, 242; Claus and Seelemann, *ibid.* 1895, [2] 52, 1). The α- acid is the less soluble and forms the less soluble barium salt; from it both a *cyano*- derivative (Jeiteles, Monatsh. 1894, 15, 807) and a *hydroxy*-derivative (Claus and Raps, *l.c.*) have been obtained by the usual methods.

(4) When heated with quinaldine, benzotrichloride and zinc chloride at 120°, it yields iso*quinoline-red* (Hofmann, Ber. 1887, 20, 9).

Physiological action.—As the physiological properties of *iso*quinoline and its derivatives proved to be identical with those of the much cheaper quinoline (Stockman, J. Physiol. 1899, 15, 245), little attention was given to the former until recently. The rapid progress of alkaloidal synthesis, however, has revived interest in the physiological study of *iso*quinoline, examples of which may be found in papers by Pyman (Chem. Soc. Trans. 1910, 97, 265), and Laidlaw (Biochem. Journ. 1911, 5, 243).

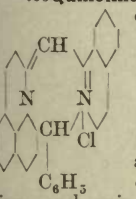
Among its derivatives are the alkaloids papaverine (Goldschmiedt, Monatsh. 1885, 6, 667), narcotine (Roser, Annalen, 1889, 254, 357), laudanosine (Pictet and Finkelstein, Ber. 1909, 42, 1979), hydrastine (Freund and Rosenberg, *ibid.* 1890, 23, 414), and berberine (Perkin, Chem. Soc. Trans. 1890, 57, 1006).

Tetrahydro*iso*quinoline is formed when *iso*quinoline is reduced with tin and hydrochloric acid (Hoogewerff and van Dorp, Rec. trav. chim. 1886, 5, 310) or with sodium and boiling alcohol (Bamberger and Dieckmann, Ber. 1893, 26, 1209), or by condensation of phenylethylamine with formaldehyde (Pictet and Spengler, *ibid.* 1911, 44, 2030).

Properties.—It is an oil, b.p. 232°–233°, absorbs carbon dioxide from the air, forms a *nitroso*- derivative, needles, m.p. 53°, an *acetyl* derivative, m.p. 46°, and in its properties shows much resemblance to benzylamine (Bamberger and Dieckmann, *l.c.*). The *hydrochloride*, B·HCl, forms prisms, m.p. 195°–197°; the *platinichloride*, $B_2 \cdot H_2PtCl_6$, prisms, m.p. 231°–232°; and the *picrate*, needles, m.p. 195°. For the 2-alkyl derivatives, *cf.* Wedekind and Oechslen, Ber. 1901, 34, 2986.

Only one colouring matter has been obtained from *iso*quinoline, namely—

*iso***Quinoline-red**, $C_{26}H_{19}N_2Cl$. This dye was obtained originally by heating benzotrichloride, benzochlorodibromide, or benzylidene chloride with a mixture of coal-tar quinoline and zinc chloride (Jacobsen, D. R.-P. 19306; 23967; Eng. Pat. 814 of 1882); and is formed by the interaction of benzotrichloride, *iso*quinoline, and quinaldine in mol. prop., either at 150°, or more rapidly in the presence of zinc chloride at 120° (Hofmann, Ber. 1887, 20, 9). The quinaldine cannot be replaced by lepidine (Vongerichten and Homann, Ber. 1912, 45, 3447).



Preparation.—A yield of 25–30 p.c. of the dye is obtained, if benzotrichloride (38 pts.) is added slowly to a mixture of *iso*quinoline (25 pts.), quinaldine (26 pts.), and zinc chloride (12·5 pts.) at 100°, and the temperature afterwards raised to 150°. Much hydrogen chloride escapes, and the reaction needs watching lest it become violent. From the extract of the product with 10 p.c. milk of lime, the unchanged bases are removed by steam, the filtrate being then acidified with hydrochloric acid to separate the dyestuff (Vongerichten and Homann, *l.c.* 3449; *cf.* Actieng. für Anilinfab., D. R.-P. 40420 of 1886).

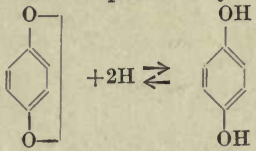
Properties.—*iso*Quinoline-red forms dark red, bronze-lustred, monoclinic prisms, which dissolve only sparingly in cold water, but readily in hot water or alcohol; these solutions are carmine-red by transmitted light, and in reflected light show a marked yellowish-red fluorescence. When heated with hydrochloric acid or with alcoholic ammonium sulphide at 200° it yields *benzaldehyde* or *benzylmercaptan* respectively, and a *base* $C_{19}H_{14}N_2$, which crystallises in plates of golden lustre, m.p. 231° (Hofmann, *l.c.*; *cf.* Vongerichten and Homann, *l.c.*). By oxidation with potassium dichromate and sulphuric acid, it furnishes *benzaldehyde* and 2-*quinolyl*-1-iso*quinolyl ketone* (Vongerichten and Krantz, Ber. 1910, 43, 129; Vongerichten and Homann, *l.c.*). As a dye-stuff it is valueless, the rose-red shades on silk or wool not being fast to light; but, mixed with cyanine, it has been used in the preparation of orthochromatic ('azaline') plates for photographic purposes (Vogel, D. R.-P. 39779 of 1886). W. P. W.

QUINOLINE DYES *v.* QUINOLINE.

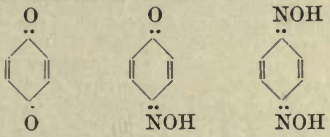
QUINOLINIC ACID *v.* BONE OIL.

QUINONE DIAZIDES (*cyclic diazo-oxides*) *v.* DIAZO COMPOUNDS.

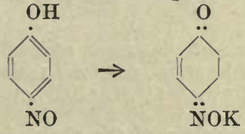
QUINONES are substances derived from aromatic hydrocarbons by replacement of two hydrogen by two oxygen atoms. The earliest known member of the series, *para*benzoquinone (or simply quinone) was obtained by the oxidation of various substituted benzenes (Woskresensky, Annalen, 1838, 27, 268; Wöhler, *ibid.* 1844, 51, 152); since it yields hexachlorobenzene when treated with phosphorus pentachloride, is easily reduced to *p*-dihydroxybenzene (quinol), and may be obtained from the latter by oxidising agents, the formula of a *p*-phenylene peroxide was assigned to it (Graebe, *ibid.* 1868, 146, 1). The relationship between quinone and quinol can then be represented by—



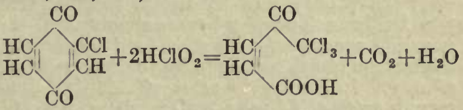
At a later date it was found that whilst benzene was reduced by free hydroxylamine, the hydrochloride gave an oxime which proved to be identical with *p*-nitrosophenol (Goldschmidt, Ber. 1884, 17, 805). The monoxime gave in turn a dioxime, these reactions pointing to the following respective formulæ for quinone, its mono- and its di- oximes.



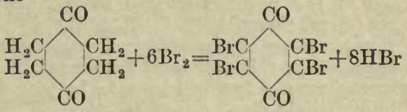
The constitution of quinone-oxime itself cannot be taken as absolutely settled; according to C. H. Sluiter (Rec. trav. chim. 1906, 25, 8), the free substance is *p*-nitrosophenol whilst the salts are derived from the quinone-oxime.



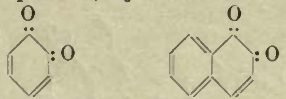
Additional support for the diketonic formula is afforded by the production of trichloroacetylacrylic acid when chlorous acid acts on benzene, quinone, &c. (Kekulé and Strecker, Annalen, 1884, 223, 170)—



and by the production of bromanil (tetrabromoquinone) from bromine and *cyclo*-hexane-1 : 4-dione



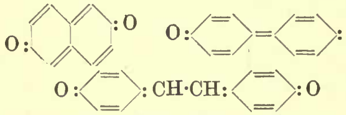
Ortho-quinones, *e.g.*



were discovered at a later date; metaquinones have not so far been obtained (R. Meyer and Desamari, Ber. 1908, 41, 2437; Zincke and Schwabe, *ibid.* 1909, 42, 797), it is doubtful whether they are capable of existence.

Within the last few years a number of

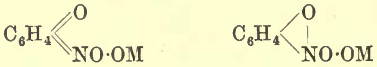
quinonoid substances have been obtained by the oxidation of dihydroxyl derivatives of aromatic compounds in which the hydroxyl groups are attached to different nuclei; *amphi*-naphthaquinone, diphenoquinone and stilbene quinone may be cited as examples. In these cases the diketonic formulæ



have the merit of simplicity when compared with the formulæ in which the two oxygen atoms are linked together.

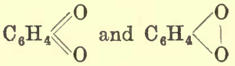
Although the diketonic has been more popular than the peroxide formula during the past 25 years, the latter is showing a revival and cannot be disregarded.

The metallic salts of the nitrophenols may be written with a quinonoïd structure which has usually been derived from the diketonic formula. Hantzsch (Ber. 1907, 40, 335) considers it at least necessary to take into account a quinonoïd structure derived from the peroxide formula



$$C_6H_4{<}\begin{array}{l}O\\NO\cdot OM\end{array}\qquad C_6H_4{<}\begin{array}{l}O\\|\\NO\cdot OM\end{array}$$

The discovery of two modifications of *o*-benzoquinone, one coloured and the other colourless, has led Willstätter and Müller (Ber. 1908, 41, 2580) to assign to them the respective formulæ

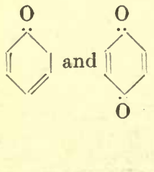


$$C_6H_4{<}\begin{array}{l}O\\O\end{array}\text{ and }C_6H_4{<}\begin{array}{l}O\\|\\O\end{array}$$

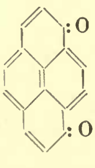
Kehrmann, however, advises caution, the colourless form has not been analysed and may be a hydrate, $O:C_6H_4:(OH)_2$ (Ber. 1911, 44, 2632).

A comparison of the absorption spectra of *p*-benzoquinone and other aromatic compounds (Hartley and Leonard, Chem. Soc. Trans. 1909, 95, 34) leads Hartley to the conclusion that the quinones must be considered as benzene derivatives (*ibid.* 58); and H. Haakh assumes that the feebly coloured *p*-benzoquinone has the peroxide constitution assigned to it by Graebe, the oxygen atoms having in this case no residual affinity. In the highly coloured additive compounds (with acids, salts, hydrocarbons, phenols, &c.), the quinone is supposed to acquire the diketonic constitution, addition occurring in virtue of the residual affinity of the oxygen atoms (J. pr. Chem. 1910, ii. 82, 546).

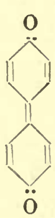
For purposes of classification, quinones will be regarded in this article as homonuclear and heteronuclear; a few will have to be placed in an intermediate class, *e.g.*



o- and *p*-Benzoquinones.



Pyrene-quinone.



Diphenoquinone.

Occasionally the term 'quinone' is applied to compounds containing two carbonyl groups in a five-membered ring (*e.g.* acenaphthenequinone), and several heterocyclic compounds containing two carbonyl groups (alloxan, isatin, &c.) exhibit many of the properties of quinones. Meanwhile hydroxypyridine quinone has been obtained by Peratoner and Tamburello (Gazz. chim. ital. 1911, 41, ii. 619).

HOMONUCLEAR QUINONES.

GENERAL METHODS OF PREPARATION.

(1) By the oxidation of *o*- and *p*-dihydroxy-derivatives of aromatic hydrocarbons. 1 : 2 : 4-trihydroxy-compounds might give *o*- or *p*-quinones; the *p*-quinonoïd configuration is usually favoured, but 2-hydroxy-1 : 4-naphthaquinone and 4-hydroxy-1 : 2-naphthaquinone appear to be tautomeric.

(2) By the oxidation of aromatic hydrocarbons, their hydroxy-, amino-, *p*-hydroxy-amino-derivatives, &c.

(3) By the acid hydrolysis of indophenols (the compounds resulting from the oxidation of mixtures of phenols and *p*-diamines).

$$C_6H_5OH+NH_2\cdot C_6H_4\cdot N(CH_3)_2+2O$$
$$=2H_2O+O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2$$
$$O:C_6H_4:N\cdot C_6H_4\cdot N(CH_3)_2+H_2O$$
$$=O:C_6H_4:O+NH_2\cdot C_6H_4\cdot N(CH_3)_2$$

(Bayrac, Bull. Soc. chim. 1894, iii. 11, 1129).

(4) By warming diketones of the type $CH_3\cdot CO\cdot CO\cdot R$ with dilute sodium hydroxide

$$2CH_3\cdot CO\cdot CO\cdot CH_3=2H_2O+C_6H_2(CH_3)_2O_2.$$

(von Pechmann, Ber. 1888, 21, 1417).

PROPERTIES AND GENERAL REACTIONS.

(1) The quinones are solid at ordinary temperatures, generally volatile with steam and are coloured.

(2) Easily reduced to dihydroxy-aromatic compounds. The latter, when cautiously oxidised, furnish quinhydrones as intermediate products; these may also be obtained by careful reduction of quinones.

(3) Quinones easily form additive compounds. Besides the quinhydrones, additive compounds may be obtained with aromatic hydrocarbons, bases, metallic salts, &c. (*see* below *Addition compounds of quinones*).

(4) Quinones react with many compounds RH to furnish R-substituted quinols

$$C_6H_4O_2+RH=C_6H_3R(OH)_2.$$

In reactions of this kind

$$R=Cl,Br,\cdot SO_3K,C_6H_5\cdot SO_2,\ \&c.$$

Wöhler found that quinone and hydrogen chloride give chloroquinol (Annalen, 1844, 51, 155). Difficulty has been found in accepting Thiele's theory of the addition process (*ibid.* 1899, 306, 133), owing to the intermediate production of quinhydrone, first observed by Staedeler (*ibid.* 1849, 69, 308). Schmidlin has shown that this is no real objection and Thiele's theory may be accepted (Ber. 1911, 44, 1700; *see Addition compounds of quinones* for a discussion).

(5) Quinones are easily chlorinated and generally the chlorine may be partially replaced by hydroxyl.

(6) Ammonia and amines yield amino-substituted quinones, with simultaneous reduction of a portion of the quinone

$$3C_6H_4O_2+2C_6H_5NH_2 \\ =C_6H_2(NHC_6H_5)_2O_2+2C_6H_4(OH)_2.$$

Dry quinones do not absorb dry ammonia (Hantzsch and Dollfus, Ber. 1902, 35, 241).

Compounds of the types $C_6H_4(:NR):O$ and $C_6H_4(:NR)_2$ are obtained by indirect means; usually by oxidising amino-phenols, *p*-diamines and their derivatives. Compounds such as $O:C_6H_4:N{\cdot}C_6H_4{\cdot}NH_2$ and

$$NH:C_6H_4:N{\cdot}C_6H_4{\cdot}NH_2$$

(as well as their alkyl derivatives) are known as indophenols and indamines (*q.v.*) respectively.

(7) Free hydroxylamine reduces quinones to quinols; with hydroxylamine hydrochloride oximes are produced.

$$C_6H_4O_2 \rightarrow C_6H_4O(:NOH) \rightarrow C_6H_4(:NOH)_2.$$

Quinone monoximes are also formed by the action of nitrous acid on phenols

$$C_6H_5OH+HO{\cdot}NO=H_2O+C_6H_4(OH)(NO)$$
or
$$C_6H_4(:O)(:NOH)$$

The dioximes are oxidised to *p*-dinitroso or *p*-dinitro-derivatives of the hydrocarbons by potassium ferricyanide or fuming nitric acid respectively.

(8) The chloro-imines corresponding to the oximes are obtained by the action of chloride of lime solution on the hydrochlorides of the *p*-aminophenols and the *p*-diamines.

$$NH_2{\cdot}C_6H_4{\cdot}OH+2Cl_2=3HCl+ClN:C_6H_4:O$$
$$NH_2{\cdot}C_6H_4{\cdot}NH_2+3Cl_2=4HCl+ClN:C_6H_4:NCl.$$

The monochloroimines react with tertiary amines giving indophenols.

$$C_6H_4O(:NCl)+C_6H_5{\cdot}NR_2 \\ =HCl+O:C_6H_4:N{\cdot}C_6H_4{\cdot}NR_2.$$

(9) By magnesium alkyl halides, pseudoquinols, *e.g.* $O:C_6H_2(CH_3)_2{<}\genfrac{}{}{0pt}{}{CH_3}{OH}$ are produced (Bamberger and Blangey, Ber. 1903, 36, 1625).

(10) Quinones react with one or two molecules of ketenes, the β-lactones obtained in this way lose carbon dioxide if heated under certain conditions, and quinomethanes or quinodimethanes are formed.

$$O{:}C_6H_4{<}\frac{C(C_6H_5)_2}{O}{>}CO=CO_2+O{:}C_6H_4{:}C(C_6H_5)_2$$

$$CO{<}\frac{C(C_6H_5)_2}{O}{>}C_6H_4{<}\frac{C(C_6H_5)_2}{O}{>}CO \\ =2CO_2+(C_6H_5)_2C:C_6H_4:C(C_6H_5)_2.$$

Under other conditions, the mono-β-lactones undergo intramolecular rearrangement with production of γ-lactones

$$O:C_6H_4{<}\frac{C(C_6H_5)_2}{O}{>}CO \\ =HO{\cdot}C_6H_3{<}\frac{C(C_6H_5)_2}{O}{>}CO$$

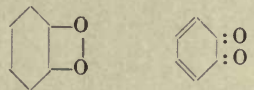
(Staudinger and Bereza, Annalen, 1911, 380, 243).

QUINONES $C_nH_{2n-8}O_2$.

o-**Benzoquinone** $C_6H_4O_2$ is obtained in chloroform solution by the action of iodine on the lead derivative of catechol (Jackson and Koch, Amer. Chem. J. 1901, 26, 21), and can be isolated in a solid condition when catechol dissolved in an indifferent solvent (*e.g.* dry ether) is treated with silver oxide (Willstätter and Müller, Ber. 1908, 41, 2580). Working rapidly with small quantities of materials, the compound may be obtained as colourless prisms; working more slowly a stabler, bright-red form is obtained.

The colourless modification either changes into the red form on keeping or decomposes. It frequently explodes when rubbed, liberates iodine immediately from acidified potassium iodide, turns guiacum tincture blue, and oxidises hydrocoerulignone. It is reduced by sulphurous acid to catechol.

The red modification is more soluble in ether; it is formed by spontaneous transformation of the colourless variety. There is apparently an equilibrium between the two modifications, as a small amount of the colourless variety is usually produced when the red modification is recrystallised. According to Willstätter and Müller, the two forms may be represented structurally thus:—



Colourless. Red.

Kehrmann suggests that the colourless modification is a hydrate (Ber. 1911, 44, 2632).

Diimine $C_6H_4(NH)_2$. Known only in solution. After adding acid, diaminophenazine and 2:2′-diaminoazobenzene may be isolated (Willstätter and Pfannenstiehl, Ber. 1905, 38, 2348).

Monoxime $C_6H_4O(:NOH)$. Obtained as an oil by the hydrolysis of *o*-nitrosoanisole (Baeyer and Knorr, *ibid.* 1902, 35, 3037; see also, Baudisch and Karzeff, *ibid.* 1912, 45, 1164).

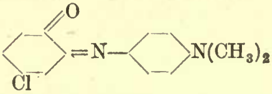
Dioxime $C_6H_4(:NOH)_2$, m.p. 142°. By the action of hydroxylamine on *o*-dinitrosobenzene (Zincke and Schwarz, Annalen, 1899, 307, 39; compare Green and Rowe, Chem. Soc. Trans. 1912, 101, 2447). Gives phenylenefurazane $C_6H_4{\lessgtr}\genfrac{}{}{0pt}{}{N}{N}{>}O$ when boiled with acetic anhydride.

o-Benzoquinone and α-benzoylphenylhydrazine give *o*-benzoxyazobenzene (m.p. 93°), and not the isomeric quinonehydrazone (McPherson and Lucas, J. Amer. Chem. Soc. 1909, 31, 281).

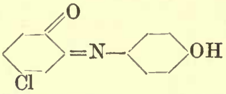
3-Chloro-*o*-benzoquinone $C_6H_3ClO_2$. By oxidation of 3-chlorocatechol with lead peroxide in suspension in ether and petroleum ether. Red crystals, discolours at 63°, decomposes at 68° (Willstätter and H. E. Müller, Ber. 1911, 44, 2189).

4-Chloro-*o*-benzoquinone. From 4-chlorocatechol dissolved in ether with silver oxide. Red crystals, m.p. 78° (Willstätter and Müller).

The only indophenols of the ortho- series which have been described, are derivatives of this quinone. Even in this case it is doubtful whether the chlorine atom has not been displaced and the indophenols obtained do not really belong to the *para* series (Friedländer, Fortschritte der Theerfarben-fabrikation, viii. 494). Attempts at preparing indophenols, using *p*-cresol and phenol-*p*-sulphonic acid, have been without result, but indophenols are formed when *p*-chlorophenol is oxidised along with a *p*-diamine or a *p*-aminophenol. To the resulting compounds, structures such as



and



have been assigned (Meister, Lucius and Brüning, D. R. P. 158091, 1903).

A solution of dimethyl-*p*-phenylene diamine in 15,000 parts of water prepared from 150 parts of nitrosodimethylaniline, 86 parts of concentrated hydrochloric acid, and 186 parts of zinc dust is mixed with 140 parts of crystallised *p*-chlorophenol, 120 parts of soda-lye, and 212 parts of sodium carbonate in 12,000 parts of water. 1318 parts of potassium ferricyanide in 3500 parts of water are then run in and the indophenol separates out at once. It dissolves in alcohol with a blue colour, which becomes redder in shade on addition of acids. It dissolves easily in sodium sulphide solution as the leuco- compound. In place of ferricyanide, hypochlorites may be used for the oxidation.

Both the indophenol and its leuco- compound, when heated with alkaline polysulphides, give a blue colouring matter; addition of copper at the same time causes the formation of a green dye.

To prepare the hydroxyindophenol, 11 parts of *p*-aminophenol, 60 parts of water, and 10 parts of 40 p.c. hydrochloric acid are mixed with 13 parts of *p*-chlorophenol and 33 parts of caustic soda-lye of 40°Bé. in 100 parts of water. This mixture is run into a second mixture made from 290 parts of sodium hypochlorite solution (containing 49 grams of active chlorine per kilogram), 200 parts of sodium chloride, and 200 parts of ice. The sodium salt of the oxidation product separates as a green crystalline mass. The aqueous solution is reddened by acetic acid; concentrated sulphuric acid gives a deep blue solution.

4 : 5-Dichloro-*o*-quinone $C_6H_2Cl_2O_2$, m.p. 94°. By oxidising 4 : 5-dichloro-catechol dissolved in ether with silver oxide (Willstätter and Müller).

Tetrachloro-*o*-quinone $C_6Cl_4O_2$, m.p. 129°–130°. By oxidation of tetrachlorocatechol with nitric acid, or by the action of chlorine on catechol dissolved in hot acetic acid (Zincke, Ber. 1887, 20, 1779; 1888, 21, 2730; Cousin, Compt. rend. 1899, 129, 967; Jackson and MacLaurin, Ber. 1905, 38, 4103).

Tetrabromo-*o*-quinone $C_6Br_4O_2$, m.p. 150°–151°. By oxidation of tetrabromocatechol with bromine (Stenhouse, Annalen, 1875, 177, 197), chlorine or nitric acid (Zincke, Ber. 1887, 20, 1777). Thick dark red prisms or tablets. Acts as an oxidising agent. Yields dibromodianilino-*o*-quinone, m.p. 160°, when treated with aniline (Jackson and Porter, *ibid.* 1902, 35, 3851). Sodium hydroxide gives tetrabromocatechol and a *cyclo*-pentadiene derivative (Jackson and Fiske, *ibid.* 1909, 42, 2636). For other reactions, *see* Cousin (*l.c.*) and Jackson and Russe (Ber. 1905, 38, 419; Amer. Chem. J. 1906, 35, 154).

3-Hydroxy-*o*-benzoquinone $C_6H_3(OH)O_2$, m.p. 206°–208°. Colourless prismatic needles by acting on an alcoholic solution of pyrogallol with amyl nitrite and acetic acid. *Acetyl derivative*, m.p. 273° (A. G. Perkin and Steven, Chem. Soc. Trans. 1906, 89, 803).

3-Methoxy-*o*-benzoquinone $C_6H_3(OCH_3)O_2$. Dark red crystals, m.p. 115°–120° (Willstätter and F. Müller, 1911, 44, 2179).

3 : 5 : 6-Trichloro-4-methoxy-*o*-benzoquinone $C_6Cl_3(OCH_3)O_2$, m.p. 93°–94°. By oxidation of 3 : 5 : 6-trichloro-2 : 4-dimethoxyphenol. Hydrolysed to trichlorohydroxy-*p*-benzoquinone (Zincke and Schaum, Ber. 1894, 27, 555).

***p*-Benzoquinone** (*quinone*), $C_6H_4O_2$. Obtained by the action of chromic acid mixture on quinic acid (Woskresensky, Annalen, 1838, 27, 268), quinol (Wöhler, *ibid.* 1844, 51, 152), aniline, benzidine (Hofmann, Jahresb. 1863, 415), *p*-phenylenediamine (*ibid.* 422), sulphanilic acid (Meyer and Ador, Annalen, 1871, 159, 7; Schrader, Ber. 1875, 8, 760), phenol-*p*-sulphonic acid (Schrader), arbutin (Strecker, Annalen, 1858, 107, 233), various plant constituents (Stenhouse, *ibid.* 1854, 89, 247), aniline black (Nietzki, Ber. 1877, 10, 1934). By decomposition of the compound $C_6H_4(CrO_2Cl)_2$ with water (Etard, Ann. Chim. Phys. 1881, v. 22, 270), by hydrolysis of certain indophenols (*v. supra*), by the fermentation of fresh grass (Emmerling, Ber. 1897, 30, 1870), by oxidation of betite, $C_6H_{12}O_4$ (v. Lippmann, *ibid.* 1901, 34, 1162), by the action of iodine on the lead derivative of quinol (Jackson and Koch, *ibid.* 1898, 31, 1458; Amer. Chem. J. 1901, 26, 20) and by the electrolytic oxidation of aniline or benzene in acid solution salts of chromium, manganese, or vanadium being present.

Bamberger and Tschirner indicate that phenylhydroxylamine and *p*-aminophenol are intermediate products in the oxidation of aniline to quinone (Ber. 1898, 31, 1624). The theory of the formation of quinone from aniline is also dealt with by Willstätter and Dorogi (*ibid.* 1909, 42, 2147).

PREPARATION OF *p*-BENZOQUINONE.

(*a*) By oxidation of aniline with chromic acid. According to Nietzki's directions (Ber. 1886, 19, 1468; *see* also Annalen, 1882, 215, 127), a concentrated solution of sodium dichromate is added to a well-cooled solution of 1 part of aniline in 25 parts of water and 8 parts of sulphuric acid. The quinone is subsequently extracted by ether. For modified methods of oxidising aniline, quinol, &c., see Seyda (Ber. 1883, 16, 687), Schniter (*ibid.* 1887, 20, 2283), Hesse (Annalen, 1880, 200, 240), Sarauw (*ibid.* 1881, 209, 99), Clark (Amer. Chem. J. 1892, 14, 555).

(*b*) By anodic oxidation of aniline in a cooled solution of chromium sulphate and sulphuric acid. The liquid is continually agitated during the process (F. Darmstädter, D. R. P. 109012, 1897).

(*c*) By anodic oxidation of aniline or quinol in sulphuric acid in presence of manganese sulphate. The outer cathode cell contains 20 p.c. sulphuric acid, a lead electrode and a porous earthenware vessel which serves as the anode cell; as anode a lead cylinder is used. A mixture of 25 parts by weight of manganese sulphate, 100 parts by weight of water and 10 parts by weight of concentrated sulphuric acid are placed in the anode cell, the whole apparatus thoroughly cooled and a current of 175 ampères per square metre passed until about half of the manganese sulphate is oxidised: care is necessary to prevent the temperature rising above 0° in the anode cell. A well cooled solution of 20 parts by weight of aniline in 300 parts by weight of water and 160 parts by weight of concentrated sulphuric acid is then added to the contents of the anode cell which is well stirred and the current passed until all the aniline black is oxidised. In making quinone from quinol, 30 parts by weight of the latter in 300 of water and 160 of concentrated sulphuric acid are added and the current passed until the dark-green quinhydrone disappears (C. F. Boehringer und Söhne, D. R. P. 117129, 1899).

(*d*) By anodic oxidation of aniline in presence of vanadic acid. A quantitative employment of the anodic oxygen is claimed when sulphuric acid of 10 p.c. strength to which 3 p.c. of vanadic acid (calculated on the sulphuric acid) has been added. The temperature is kept at 5°–10°; E.M.F., 3–4 volts; current density, 400 ampères per square metre. For a good yield it is well to add the aniline in small quantities (Meister, Lucius and Brüning, D. R. P. 172654, 1903).

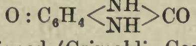
(*e*) Preparation of *p*-benzoquinone and quinol by the electrolytic oxidation of benzene. Benzene when emulsified with dilute sulphuric acid is oxidised to quinone by lead peroxide; on the other hand quinone may be reduced to quinol cathodically. Since lead peroxide is produced on a lead anode the two operations may be combined if a cell with a diaphragm is used. A lead disc which has been coated mechanically or electrically with peroxide serves as the anode and is rapidly rotated in a narrow glass cell, the anode space containing 150 c.c. of 10 p.c. sulphuric acid and 90 c.c. of benzene. The current is about 1 ampère per square decimetre, E.M.F. 4 volts. The quinone, as produced, dissolves in the excess of benzene. If the mixture of dilute acid and benzene solution of quinone be then transferred to the cathode cell, the quinone is reduced to quinol which passes into the dilute sulphuric acid. It may be extracted from the solution with ether, whilst the excess of benzene may be returned to the anode cell (Kempf, D. R. P. 117251, 1899; Zeitsch. Electrochem. 1901, 7, 592; J. pr. Chem. 1911, ii. 83, 329).

p-Benzoquinone forms long, yellow, monoclinic prisms. It sublimes in gold coloured needles; the odour is penetrating and reminiscent of the halogens. Slightly soluble in cold, easily in hot water as also in alcohol and ether; fairly soluble in boiling petroleum spirit: m.p. 115·7°; sp.gr. 1·307–1·318; molecular heat of combustion at constant pressure, 658·4 cal. (Valeur, Ann. Chim. Phys. 1900, vii. 21, 475; Berthelot and Recoura found 656·8 cal. (*ibid.* 1888, vi. 13, 312; *see* also Compt. rend. 1897, 125, 872).

Quinone dissolves in cold concentrated nitric acid without change; on heating, oxalic acid is formed (Schoonbroodt, Bull. Soc. chim. 1861, i. 3, 107; Sertini, Gazz. chim. ital. 1902, 32, i. 322). Heated by itself to 160°, or with water in a sealed tube to 100°, quinol and quinhydrone are formed (Scheid, Annalen, 1883, 218, 227; *see* also action of aqueous sodium acetate; Hesse, *ibid.* 1883, 220, 367). Quinone, especially when exposed to light (Ciamician, Gazz. chim. ital. 1886, 16, 111; Ciamician and Silber, Rendiconti d. R. Accad. d. Lincei, 1901 [v.] 10, i. 93) acts as an oxidising agent. An alkaline solution of quinone, however, absorbs oxygen from the air.

Quinone gives addition products with one or two molecules of chlorine or bromine (Clark, Amer. Chem. J. 1892, 14, 357, 556; Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 384; Sarauw, Annalen, 1881, 209, 111; Nef, J. pr. Chem. 1890, ii. 42, 182), and with metallic chlorides, *e.g.* $C_6H_4O_2\cdot SnCl_4\cdot C_6H_6$ (K. H. Meyer, Ber. 1908, 41, 2568). The addition products with phenols, &c., are dealt with under a separate heading.

Hydrogen chloride is added with formation of chloroquinol; the action of hydrogen bromide is somewhat similar. Various compounds are produced by the action of phosphorus trichloride and phosphoryl chloride (Scheid, Annalen, 1883, 218, 198). Quinone and ammonia gas give 'quinone amide,' $3C_6H_4O_2\cdot NH_3$ (?) (Woskresensky, Ber. Jahresbericht. 26, 801). The action of ammonia in presence of solvents has been studied by Knapp and Schultz (Annalen, 1881, 210, 178) and by Hebebrand and Zincke (Ber. 1883, 16, 1556). Carbamide at 150° gives a monoureïde to which the constitution



$$O:C_6H_4<{}^{NH}_{NH}>CO$$

has been assigned (Grimaldi, Gazz. chim. ital. 1895, 25, i. 79; 1897, 27, i. 240).

Quinone reacts with many compounds containing the amino-group, *e.g.* anthranilic acid, *o*-nitroaniline (Hebebrand, Ber. 1882, 15, 1976; Leicester, Chem. News, 1896, 74, 236), *p*-nitroaniline (Hebebrand), diamino-diphenylmethane, &c. (Siegmund, J. pr. Chem. 1910, ii. 82, 409). Free hydroxylamine acts as a reducing agent; the hydrochloride yields either the mono- or the di-oxime. Phenylhydrazine and $\alpha\alpha$-phenylbenzylhydrazine are oxidised by quinone, but $\alpha\alpha$-phenylbenzoylhydrazine yields a hydrazone $(C_6H_5)(C_7H_5O)N\cdot N:C_6H_4:O$, which gives benzeneazophenol on hydrolysis. The compound is, however, isomeric with the ester obtained by the direct benzoylation of the azophenol (McPherson, Ber. 1895, 28, 2415; Amer. Chem. J. 1899, 22, 366, 377). Quinone and its monoxime condense normally with hydrazides of the type $R\cdot CO\cdot NH\cdot NH_2$ (Borsche, Annalen, 1905, 343, 176).

Anhydrous hydrogen cyanide is without action on quinone (Levy and Schultz, Annalen, 1881, 210, 143), but the nascent acid gives 2:3-dicyanoquinol (Thiele and Meisenheimer, Ber. 1900, 33, 675; Bayer and Co., D. R. P. 117005, 1899).

Diazomethane gives a compound from which 1:4-diketobenzo*bis*-dihydropyrazole can be obtained (v. Pechmann and Seel, Ber. 1899, 32, 2295). Phenylazoimide reacts with quinone yielding quinhydrone, 4:7-diketo-1-phenyl-1:2:3-benztriazole (m.p. 180–184°), 4:8-diketo-1:5-diphenylbenzditriazole (decomposes about 340°), 4:8-diketo-1:7-diphenylbenzditriazole (m.p. 280–285°), and a yellow substance, $C_{10}H_{14}O_2N_4$ (m.p. 157°), of unknown constitution (Wolff and Grau, Annalen, 1912, 394, 68). In presence of zinc chloride, primary alcohols give 2:5-dialkyl-1:4-quinones (Knoevenagel and Bückel, *ibid.* 1901, 34, 3993); with resorcinol in acetic acid solution, 1 : 4 : 3′-trihydroxydiphenyl ether is produced on addition of a few drops of dilute sulphuric acid: α-naphthol gives a similar reaction (Friedländer and Blumenfeld, *ibid.* 1897, 30, 1464, 2568; D. R. P. 96565, 1897). Boiled with anthranol in nitrobenzene solution, a compound, $C_{20}H_{10}O_3$ (black powder), is produced (Meister, Lucius and Brüning, D. R. P. 251020). Benzhydrol condenses with quinone in a mixture of acetic and sulphuric acids to benzoquinone-*bis*-diphenylmethane (Möhlau and Klopfer, Ber. 1899, 32, 2147). Möhlau regarded this reaction as characteristic of quinonoid compounds. Aromatic aminohydroxy acids gives quinoneimide mordant dyestuffs (v. Heyden, D. R. P. 119863, 1898).

Acetaldehyde unites with quinone on exposure to sunlight giving acetoquinol (Klinger and Kolvenbach, Ber. 1898, 31, 1214). With ethyl acetoacetate and zinc chloride, the ethyl esters of *p*-hydroxybenzo-α-methylfurane carboxylic acid, $C_{10}H_7O_4{\cdot}C_2H_5$, and benzo-dimethyl-*p*-difurane-dicarboxylic acid, $C_{14}H_8O_6(C_2H_5)_2$, are produced.

Buschka (Ber. 1881, 14, 1327) and Sarauw (Annalen, 1881, 209, 129) both obtained diacetylquinol from quinone and acetic anhydride, acetyl chloride gave the diacetyl derivatives of chloroquinol, dichloroquinol, and quinol (small amount). Thiele finds that acetic anhydride in presence of concentrated sulphuric acid gives 1 : 2 : 4-triacetoxybenzene (Ber. 1898, 31, 1247). To carry out this reaction technically, 15 kilos. of quinone are added gradually to a mixture of 40–45 kilos. of acetic anhydride and 1 kilo. of concentrated sulphuric acid. The mixture becomes hot and the quinone dissolves: the temperature should be kept at 40°–50°. When no further heat development is observed, the triacetoxybenzene is precipitated by pouring into water (Bayer and Co., D. R. P. 101607, 1897). A modified process is to add 10 kilos. of quinone to 30–40 kilos. of acetic anhydride in which 0·5 kilo. of crystallised phosphoric acid has been dissolved. Reaction takes place at the ordinary temperature and requires several days for completion (Bayer and Co., D. R. P. 107508, 1898).

Quinone and 'triphenylmethyl' give quinol-triphenylmethyl ether, $C_6H_4[O{\cdot}C(C_6H_5)_3]_2$; m.p. 241° (Schmidlin, Wohl and Thommen, Ber. 1910, 43, 1298).

The action of potassium and its ethoxide towards quinone has been studied by Astre (Bull. Soc. chim. 1895, iii. 13, 1037, 1070). By leading oxygen through warm solutions of quinone in alcoholic potash the salts KHC_6O_6 and $K_2C_6O_6$ are produced. On adding concentrated alcoholic potash to a dilute ethereal solution of quinone, a decomposable, blue, crystalline salt, $KC_6H_3O_2{\cdot}H_2O$, is precipitated.

Hydrogen sulphide reduces quinone to quinol. Wöhler also obtained compounds, $C_{12}H_{10}O_4S_2$ (?) and $C_{12}H_{12}O_4S$ (Annalen, 1849, 69, 294). Quinone is reduced by yellow ammonium sulphide in the cold; if heated, a bluish-violet dyestuff is produced (Willgerodt, Ber. 1887, 20, 2470). Of more interest is the production of a black substantive dye, capable of technical application (Vidal, D. R. P. 84632, 1893).

A mixture of 10 kilos. of quinone, 5 kilos. of sulphur, 4 kilos. of ammonium chloride and 6 kilos. of caustic soda are heated in a closed vessel for 6 hours at 160°–210°. After cooling, the mass is crushed and can be used directly for dyeing. The solution in alkaline carbonates or sulphides has a bottle-green colour, unmordanted vegetable fibres are dyed a greenish-black; a black-blue is obtained by subsequent treatment with ferric chloride or potassium dichromate. The bottle-green alkaline solutions give a brownish-red precipitate with hydrochloric acid which blackens on exposure to the air. When the alkaline solution is oxidised in the air, a dirty green precipitate, insoluble in alkaline carbonates, is produced.

Quinone gives an indigo-coloured addition product, $2C_6H_4O_2{\cdot}H_2S_3$, with hydrogen persulphide. M. M. Richter regards this as an oxonium salt (Ber. 1910, 43, 3599).

With compounds of the type HSR, quinol derivatives, $C_6H_3(SR)(OH)_2$, are formed. These can be oxidised to quinones, $C_6H_3(SR)O_2$, which will react in turn with the sulphur compound. By alternating the reactions, all the hydrogen atoms of quinone may be replaced by SR groups. The mono-, di-, and tri-chloroquinones also react quite smoothly without the chlorine atoms being displaced. For example, the salt

$$C_6H_3(OH)_2(S{\cdot}SO_3K)$$

may be obtained by mixing 43·2 parts of quinone in 150 parts of glacial acetic acid with 150 parts of sodium thiosulphate in 200 parts of water and salting out with potassium chloride. If the salt is reduced by zinc dust and acid in presence of ether, thiolquinol, $C_6H_3(SH)(OH)_2$, m.p. 119°–120°, is obtained. Other compounds containing the group .SH (or .SM) which have been employed are thiobenzoic acid, potassium xanthogenate, potassium thiocyanate and sodium trithiocarbonate (Badische Anilin- und Soda-Fabrik, D. R. P. 175070, 1905).

The compounds obtained according to the foregoing method may be used for the manufacture of sulphur dyes. The necessary materials are (1) benzoquinone or one of its halogen derivatives, (2) a compound containing the group SR, (3) a *mono-* or *as-di-*alkylated *p*-diaminethiosulphonic acid or the corresponding mercaptan or disulphide. The following example is given in the patent (B. A. S. F., D. R. P. 167012, 1905).

25 parts of benzoquinone are dissolved in 100 parts of glacial acetic acid; the solution is cooled to 5°–10°, and a solution of 13·5 parts of sodium hydrosulphide in 60 parts of water run in. To the clear brown solution, a solution of 25 parts of dimethyl-*p*-phenylenediaminethiosulphonic acid in 200 parts of water and 15 parts of 20 p.c. ammonia is added, and then 250 parts of caustic soda lye of 40°Bé. The clear green solution is heated for 2 hours at 60° when the greater part of the colouring matter is precipitated as a dark blue powder. The filtrate from the dyestuff yields a further amount by blowing air through it. (See further, B. A. S. F., D. R. PP. 178940, 1905; 179225, 1905).

For the volumetric estimation of quinone, sulphurous acid (Nietzki, Annalen, 1882, 215, 128) or hydriodic acid and thiosulphate (A. Valeur, Compt. rend. 1899, 129, 552; Willstätter and Dorogi, Ber. 1909, 42, 2165; Wieland, *ibid.* 1910, 43, 716; Willstätter and Majima, *ibid.* 1910, 43, 1171) may be used.

Quinone-imine $C_6H_4O(:NH)$. By oxidising *p*-aminophenol in ethereal solution with silver oxide. Colourless crystals (Willstätter, Ber. 1904, 37, 1494, 4605).

Quinone-imine condenses directly with aromatic bases giving leuco-indophenols (Akt. Ges. Anilin-F., D. R. P. 184601, 1905)

$$O:C_6H_4:NH+C_{10}H_7{\cdot}NH_2 =HO{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_7{\cdot}NH_2.$$

A cold aqueous solution of quinone-imine, obtained from 14·6 kilos. of *p*-aminophenol and the calculated amount of ferric chloride, is mixed with a concentrated solution of 18 kilos. of *α*-naphthylamine hydrochloride. The leuco-indophenol separates immediately and is filtered off and washed. It may be used directly in the preparation of sulphur dyestuffs.

Quinone-chloroimine $C_6H_4O(:NCl)$, is obtained from *p*-aminophenol or *p*-phenetidine and bleaching powder solution (Schmitt and pupils, J. pr. Chem. 1873, ii. 8, 2; 1878, ii. 19, 315; 1881, ii. 23, 435; Hirsch, Ber. 1880, 13, 1903). Willstätter and Mayer use a solution of sodium hypochlorite and *p*-aminophenol hydrochloride (Ber. 1904, 37, 1499). Bamberger and Tschirner obtained it mixed with other products by the action of hypochlorous acid on aniline (*ibid.* 1898, 31, 1523).

Quinone-chloroimine forms yellow crystals, m.p. 85°, explodes on further heating. Volatile with steam, easily soluble in organic solvents and hot water, difficultly in cold. Hydrolysed to ammonium chloride and quinone, reduced to *p*-aminophenol, soluble in cold concentrated sulphuric acid and fuming nitric acid without decomposition. Yields mono-, di-, and tri-chloroaminophenols with concentrated hydrochloric acid. Used for synthetic purposes and in the preparation of dyestuffs (Clayton Aniline Co., D. R. P. 106036, 1898; Akt. Ges. Anilin-F., D. R. P. 124872, 1899).

An example of the preparation of a black sulphur dyestuff is taken from a subsequent patent.

10 parts of quinone-chloroimine are suspended in a concentrated solution of 15·5 parts of sodium thiosulphate; 240 parts of 33 p.c. sulphuric acid are added in the cold and the mixture slowly warmed. The colour of the solution becomes reddish-brown, then black-brown: finally the mixture is boiled for 1 or 2 hours. After cooling, the precipitate is collected, washed, dissolved in dilute caustic soda or sodium carbonate and salted out. The alkaline solutions have a brownish-black shade. A similar dyestuff may be obtained from chloroquinone-chloroimine (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

Quinone chloroimine condenses with aromatic amines and phenols, giving indophenols. The reaction can be carried out when the chloroimine is dry or in paste. Examples are given using *α*-naphthol, *α*-naphthylamine, *o*-toluidine and diphenylamine (Weiler-ter-Meer, D. R. P. 189212, 1906, lapsed in 1909).

Quinone-methylimine $C_6H_4O(:NCH_3)$. By oxidising *p*-methylaminophenol dissolved in ether with silver oxide or lead peroxide. Explosive needles (Willstätter and Pfannenstiehl. Ber. 1905, 38, 2244).

Quinone-phenylimine $C_6H_4O(:N{\cdot}C_6H_5)$. By oxidising *p*-hydroxydiphenylamine dissolved in benzene with yellow mercuric oxide, m.p. 97° (Bandrowski, Monatsh. 1888, 9, 134).

*Quinone-*p*-tolylimine* $C_6H_4O(:N{\cdot}C_6H_4{\cdot}CH_3)$, m.p. 70° (Bandrowski).

*Quinone-*p*-anisylimine*

$$C_6H_4O(:N{\cdot}C_6H_4{\cdot}OCH_3),$$

m.p. 84° (Willstätter and Kubli, Ber. 1909, 42, 4135).

The violet colouring matter obtained by oxidising *p*-aminophenol with ferric chloride appears to possess the constitution

$$C_6H_3(OH)(NH_2){\cdot}N:C_6H_4:O,HCl$$

(Willstätter and Piccard, Ber. 1909, 42, 1902). The indophenols (*q.v.*) may be regarded as derivatives of the quinone arylimines or aryldiimines; their structure is represented by $O:C_6H_4:N{\cdot}C_6H_4{\cdot}NH_2$ or $HO{\cdot}C_6H_4{\cdot}N:C_6H_4:NH$.

Quinone-diimine $C_6H_4(:NH)_2$. By oxidising *p*-phenylenediamine in ethereal solution with silver oxide (Willstätter and Pfannenstiehl, Ber. 1904, 37, 4606), or by passing ammonia into an ethereal suspension of the dihydrochloride. Colourless crystals, discoloured at 75°, m.p. 124°. Explodes with concentrated sulphuric acid unless mixed carefully. *Dihydrochloride*, colourless when pure, is produced by passing hydrogen chloride into a solution of the diimine in ether or benzene, or from quinone-dichlorodiimine and hydrochloric acid (Willstätter and Meyer, *ibid.* 1904, 37, 1494). *See* also Pringsheim, *ibid.* 1905, 38, 3354; Kehrmann, *ibid.* 3777). *Monohydrobromide*, from bromine on ethereal *p*-phenylene diamine (Jackson and Calhane, 1902, 35, 2496) is probably a 'meriquinonoïd' compound. *Di-*p*-nitrophenolate* $C_6H_4(:NH_2{\cdot}O{\cdot}C_6H_4{\cdot}NO_2)_2$, m.p. 59°; pale coloured (A. Knorr, Ber. 1911, 44, 1503).

The quinone-diimines may be used directly for the preparation of leuco-indophenols (Akt. Ges. Anilin-F., D. R. P. 184651, 1905). The solution obtained by oxidising 13·6 kilos. of dimethyl-*p*-phenylenediamine with ferric chloride is added to a solution of 9·4 kilos of phenol. in water, stirring and cooling meanwhile. The leucoindophenol separates rapidly; the precipitation is completed by salting out.

The solution of quinone-diimine-sulphonic acid obtained by oxidising 18·8 kilos. of *p*-phenylenediamine-sulphonic acid with ferric chloride is allowed to flow into a cooled solution of 10·8 kilos. of *o*-cresol. A precipitate is produced: it is soluble in alkalis.

Quinone-dichlorodiimine $C_6H_4(:NCl)_2$. By adding to a solution of *p*-phenylenediamine hydrochloride, a solution of bleaching powder (Krause, Ber. 1879, 12, 47) or sodium hypochlorite (Willstätter and E. Meyer, *ibid.* 1904, 37, 1498). Volatile with steam, soluble in organic solvents, m.p. 126° (with decomposition). Reduced by stannous chloride, sulphurous acid and sodium amalgam to *p*-phenylene diamine. With hydrochloric acid gives quinone-diimine dihydrochloride or tetrachloro-*p*-phenylenediamine. Used synthetically, *e.g.* the compound $C_{10}H_6{<}^{O}_{N}{>}C_6H_3:NH$ is produced on condensation with *β*-naphthol (Nietzki and Otto, Ber. 1888, 21, 1745). Has been employed in the production of indophenols, azines (Bayer and

Co., D. R. P. 84504, 1894) and sulphur dyestuffs.

Whilst most of the *indophenols* have not been used to a large extent for dyeing, they have proved to be useful materials in the preparation of sulphur dyestuffs. This holds good for their leuco-compounds, the 4 : 4′-aminohydroxy-derivatives of secondary aromatic amines. The indophenols were first prepared by the action of nitrosodialkylanilines on phenols (Koechlin and Witt, D. R. P. 15915, 1881; Majert, D. R. P. 18628, 1881; Cassella, D. R. PP. 18903, 1881; 19291, 1881; 20850, 1882; Bayer and Co., D. R. P. 41512, 1887). A number of patents relate to the preparation of indophenols by oxidation of a mixture of a *p*-diamine and a phenol (Akt. Ges. Anilin-F., D. R. PP. 160710, 1904; 168229, 1904; 179294, 179295, 1905); *p*-phenylenediamine-sulphonic acid may also be employed (Griesheim-Elektron, D. R. P. 171028, 1904).

For the preparation of the simplest indophenol, $NH_2{\cdot}C_6H_4{\cdot}N : C_6H_4 : O$ or

$$NH : C_6H_4 : N{\cdot}C_6H_4{\cdot}OH,$$

10·8 parts of *p*-phenylenediamine and 10 parts of phenol are dissolved in 1500 to 2000 parts of water. The solution is well stirred at 10°–15° and a paste of 48 parts of lead peroxide in a solution of 50 parts of disodium phosphate and 35 parts of sodium bicarbonate added. The indophenol is at once produced and separates in brassy leaflets (D. R. P. 179294). The phosphate and carbonate are not essential (D. R. P. 179295). 21·6 parts of *p*-phenylenediamine and 20 parts of phenol are dissolved in 3000 parts of water, stirred at 10°–15°, and a paste of 96 parts of lead peroxide added. The indophenol is extracted from the mixture with hydrated lead oxide by means of alcohol or hot water. M.p. 160°. For reactions and conversion into 7-anilinosafranol, *see* Heller, Annalen, 1912, 392, 16.

The indophenols can also be obtained from the chloroimines and monoximes of *p*-quinones by condensation with amines in presence of 70 p.c. sulphuric acid. Amino-derivatives of the indophenols are formed when *m*-diamines are used (*see* Ger. Pat. applications of Ges. Chem. Ind. Basel, A. 10389; Farbwerke Höchst, 11485).

Indophenols are obtained directly from quinone dichlorodiimine and compounds such as *α*-naphthol. A solvent is unnecessary: thus the reaction may be carried out by grinding a mixture of 164 parts of *α*-naphthol, 100 parts of the dichlorodiimine and 500 parts of common salt until the dichlorodiimine has disappeared (Weiler-ter-Meer, D. R. P. 189212, 1906, lapsed 1909).

Quinone-dichlorodiimine yields a black sulphur dye if the amount obtained from 50 parts of *p*-phenylenediamine is suspended in a concentrated solution of 100 parts of sodium thiosulphate, 1000 parts of 33 p.c. sulphuric acid added and the mixture slowly warmed (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

Quinone-dibromodiimine $C_6H_4(:NBr)_2$. Explodes at 86° (Krause, Ber. 1879, 12, 50).

Quinone monomethyldiimine

$$C_6H_4(:NH)(:N{\cdot}CH_3).$$

Colourless (Willstätter and Piccard, Ber. 1908, 41, 1458).

Quinone-s-*dimethyldiimine* $C_6H_4(:NCH_3)_2$. From *s*-dimethyl-*p*-phenylenediamine in ether with silver oxide. Colourless crystals, m.p. 92·5°–93°. Explodes with concentrated hydrochloric or sulphuric acid (Willstätter and Pfannenstiehl, *ibid.* 1905, 38, 2244). From *as*-dimethyl-*p*-phenylenediamine, Warster's 'meriquinonoïd' salt can be obtained, also a colourless imonium nitrate,

$$C_6H_4[:NH{\cdot}HNO_3][:N(CH_3)_2{\cdot}NO_3].$$

Quinone-monophenyldiimine

$$C_6H_4(:NH)(:N{\cdot}C_6H_5)$$

is obtained from *p*-aminodiphenylamine by oxidation with lead peroxide (Heucke, Annalen, 1889, 255, 193) or silver oxide (Willstätter and Moore, Ber. 1907, 40, 2665). Also by oxidation of aniline with potassium permanganate (Bamberger and Tschirner, *ibid.* 1898, 31, 1526). Brown crystals with $3CH_3OH$; m.p. 208°. The acetic acid solution has a bluish-green colour. *Polymeric form* $C_{36}H_{30}N_6$, m.p. 217°–218° (Willstätter and Kubli, Ber. 1909, 42, 4135). Quinone-phenyldiimine is of interest on account of its relation to aniline-black (*q.v.*).

Quinone-p-*tolylimine*, m.p. 114°, combines with 1 or 2 HCl *Termolecular form*, m.p. 187° (W. and K., *l.c.*).

Quinone-p-*anisylimine*, m.p. 71°–72°; *mono-* and *di-hydrochlorides*. *Termolecular form* darkens at 150°, softens at 170°, melts at 176° (W. and K.).

Quinone-mono-p-*aminophenyldiimine*

$$NH : C_6H_4 : N{\cdot}C_6H_4{\cdot}NH_2$$

is the simplest indamine. Its greenish-blue, water-soluble, unstable salts are produced by oxidising a mixture of aniline and *p*-phenylenediamine salts. An excess of mineral acid hydrolyses indamine with production of quinone. On heating with an aqueous solution of an aniline salt, phenosafranine is formed.

Bindschedler's green

$$(CH_3)_2Cl{\cdot}N : C_6H_4 : N{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

is the tetramethyl- derivative of the simplest indamine. It is produced by oxidising a mixture of dimethylaniline and dimethyl-*p*-phenylenediamine. It is of no technical importance, being easily decomposed by acid and alkalies.

Quinone diphenyldiimine $C_6H_4(:N{\cdot}C_6H_5)_2$. By oxidising diphenylamine (preferably with aniline) by potassium permanganate; shining brownish-yellow crystals, m.p. 176°–180° (Bandrowski, Monatsh. 1886, 7, 375; 1887, 8, 478). Easily reduced to diphenyl-*p*-phenylenediamine; oxidised to quinone by manganese dioxide and dilute sulphuric acid.

Quinone-monoxime $C_6H_4O(:NOH)$. By boiling nitroso-dimethylaniline with soda (Baeyer and Caro, Ber. 1874, 7, 809), by the action of nitrous acid (*ibid.* 963) or nitrosyl sulphate (Groves and Stenhouse, Chem. Soc. Trans. 1877, 32, i. 544) on phenol, by dilute solution of hydroxylamine hydrochloride on quinone (Goldschmidt, Ber. 1884, 17, 805) and by the hydrolysis of nitrosoanisole, $NO{\cdot}C_6H_4{\cdot}OCH_3$ (Baeyer and Knorr, *ibid.* 1902, 35, 3035). It is easily prepared by dissolving equivalents of phenol and sodium nitrite in water, adding a large amount of crushed ice and pouring in dilute sulphuric acid with continual stirring. The compound separates in the course of some hours, crystalline and practically pure. Modified methods of preparation are given by Hugo Koehler (D. R. P. 25469, 1883) and Nietzki and Guitermann (Ber. 1888, 21, 429).

The constitution has been already discussed; for the analogous cases of the naphthaquinone-oximes (nitrosonaphthols), *see* C. H. Sluiter (Ber. 1911, 44, 1327).

On heating, quinone-oxime decomposes at 120°–130°. Dissociation constant,

$$k=3300\times10^{-10}$$

(Hantzsch and Barth, Ber. 1902, 35, 219; *cf. ibid.* 1003). Behaviour towards ammonia (Hantzsch and Dollfuss, *ibid.* 1902, 35, 262).

Quinone-oxime gives metallic salts

$$C_6H_4O(:NOM),$$

the acyl derivatives are of type

$$C_6H_4O(:NO{\cdot}CO{\cdot}R)$$

and the alkyl compounds have a similar constitution, $C_6H_4O(:NOR)$. The isomeric nitrosophenylethers, $NO{\cdot}C_6H_4.OR$, are obtained by the action of Caro's acid on the β-alkyloxyanilines (Baeyer and Knorr, Ber. 1902, 35, 3034).

Benzoyl derivative, m.p. 172°–174° (Walker, Ber. 1884, 17, 400; Bridge, Annalen, 1893, 277, 97); *ethyl carbonate*, m.p. 109° (Walker); *phenylcarbamate*, decomposes at 110° without fusion (Goldschmidt, Ber. 1889, 22, 3105).

*Quinone-oxime-*o*-nitrophenylhydrazone*

$$C_6H_4(:NOH)(:N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)$$

From quinone-oxime and *o*-nitrophenylhydrazine; the latter will also react with quinone itself yielding *o*-nitrobenzeneazophenol. *p*-Nitrophenylhydrazine gives a hydrazone with quinone-oxime but not with quinone itself. *m*-Nitrophenylhydrazine gives neither hydroxyazo-compounds nor quinone-oxime hydrazones (Borsche, Annalen, 1904, 334, 143; 1905, 340, 85; 1906, 343, 176; 1907, 357, 171).

Quinone-oxime gives dyestuffs on heating with mineral acids. 10 parts of nitrosophenol are warmed with 100 parts of 50 p.c. sulphuric acid for 2–3 hours at 100°, the black precipitate is filtered off, washed and dried. The product is insoluble in water, cotton is coloured brown by the alkaline solution; fast shades are obtained if the dyebath contains sodium sulphide and the goods are subsequently treated with blue vitriol or bichromate solution (Clayton Aniline Co., D. R. P. 106036, 1898).

Nitrosophenol reacts with thiosulphates, this reaction forms the starting point for the sulphur dyestuff, Clayton Black D. (D. R. P. 106030, 1898).

Quinone-dioxime $C_6H_4(:NOH)_2$ is obtained by the action of hydroxylamine hydrochloride on quinone or its monoxime or on quinol (Nietzki and Kehrmann, Ber. 1887, 20, 614); on *p*-nitrosoaniline (O. Fischer and Hepp, *ibid.* 1888, 21, 685); and on benzyl-*p*-nitrosoaniline (Böddinghaus, Annalen, 1893, 263, 304). Freshly made quinone-monoxime is covered with 50 parts of water and one molecular proportion each of hydroxylamine hydrochloride and hydrochloric acid added. After standing 6–8 days, the oxime is filtered off, washed with dilute ammonia, dissolved in strong ammonia and precipitated by carbon dioxide. Needles, decomposes about 240°. Very weak acid (Farmer and Hantzsch, Ber. 1899, 32, 3107). Oxidised by alkaline ferricyanide to *p*-dinitrosobenzene. A polymerised anhydride has been described (Farmer and Hantzsch).

Two *diacetyl derivatives* are known; the *syn*-form, m.p. 147°; the *anti*-form, m.p. 190° (with decomposition) (Kehrmann, Ber. 1895, 28, 341).

Salts of a *p-dinitroxime*, *e.g.* $C_6H_4(:NO{\cdot}OK)_2$, have been obtained by reduction of *p*-dinitrobenzene (Meisenheimer, Ber. 1903, 36, 4174; 1906, 39, 2526).

Quinone in virtue of its ketonic character also yields *mono-* and *di- semicarbazones*, an *oxime-semicarbazone* and products with one or two molecules of aminoguanidine (Thiele and Barlow, Annalen, 1898, 302, 329).

2-Chloro-*p*-Benzoquinone $C_6H_3ClO_2$. By distilling copper quinate with salt, manganese dioxide and dilute sulphuric acid (Staedeler, Annalen, 1849, 69, 302). By oxidising chloroquinol with chromic acid (Levy and Schultz, *ibid.* 1881, 210, 145). From *o*-chloro-*p*-aminophenol (Kollrepp, *ibid.* 1886, 234, 14).

Pale yellow (not yellowish-red) crystals (J. Schmidlin, Ber. 1911, 44, 1700), m.p. 157°. Molecular heat of combustion at constant pressure, 618·2 cal. (A. Valeur, Ann. Chim. Phys. 1900, vii. 21, 487). Gives a dichloride and with hydrogen chloride yields 2 : 5- and 2 : 3-dichloroquinols (Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 386, 394). Reacts with bases (Niemeyer, Annalen, 1888, 228, 322, 324).

2-*Chloroquinone-4-Chloroimine*, m.p. 87° (Kollrepp). Has been used for making sulphur dyestuffs (Akt. Ges. Anilin-F., D. R. P. 127834, 1899).

2-*Chloroquinone-dichlorodiimine*, m.p. 83°–84° (Cohn, Chem. Zentr. 1902, I. 386).

2-*Chloroquinone-4-oxime* $C_6H_3ClO(:NOH)$, m.p. 141° (Kehrmann, Ber. 1888, 21, 3316; *ibid.* 1898, 303, 5; Bridge, *ibid.* 1893, 277, 100). The *methyl ether*, α- (m.p. 123°) and β- (m.p. 114°–115°), *modifications* (Bridge, *ibid.* 1893, 277, 90; Kehrmann, *ibid.* 1894, 279, 35). *α-Benzoyl derivative*, m.p. 197° (B.) or 192° (Kehrmann, Ber. 1894, 27, 218); *β-derivative*, m.p. 162° (K.). Two stereoisomeric *acetyl derivatives*, m.p. 166°–167° and 136°–137° (Kehrmann and Grah, Annalen, 1898, 303, 6).

2-*Chloroquinone-dioxime*, greyish needles (Kehrmann, Ber. 1888, 21, 3317; Kehrmann and Grah, *l.c.*). *Diacetyl derivative*, m.p. 171°–172°.

2 : 3-Dichloro-*p*-Benzoquinone $C_6H_2Cl_2O_2$, m.p. 96° (Peratoner and Genco, Gazz. chim. ital. 1894, 24, ii. 379; Oliveri, *ibid.* 1897, 27, ii. 584).

2 : 5-Dichloro-*p*-Benzoquinone. m.p. 161° (Staedeler, Annalen, 1849, 69, 309; Carius, *ibid.* 1867, 143, 316; Levy and Schultz, *ibid.* 1881, 210, 150; Möhlau, Ber. 1886, 19, 2010; Hantzsch and Schniter, *ibid.* 1887, 20, 2279; Ling, Chem. Soc. Trans. 1892, 61, 558; Bandrowski and Prokopeczko, Bull. Acad. Sci. Cracow, 1901, 441).

Compound with *m*-nitro-aniline (Niemeyer, Annalen, 1888, 228, 325); *dichlorodiimine*, m.p. 134°–135° (Möhlau); *diphenyldiimine*, m.p. 220° (Bandrowski and Prokopeczko); *monoxime* and its *acetyl derivative* (Kehrmann and Grah, Annalen, 1898, 303, 13); *dioxime* (Kehrmann).

2 : 6-Dichloro-*p*-Benzoquinone, m.p. 120°.

From 2 : 4 : 6-trichlorophenol and fuming nitric acid (Faust, Annalen, 1869, 149, 153) or by acting on an alcoholic solution of trichlorophenol with nitrous fumes (Weselsky, Ber. 1870, 3, 646). *See* also Armstrong (Zeitsch. Chem. 1871, 521); Levy (Ber. 1883, 16, 1446); Kehrmann and Tiesler (J. pr. Chem. 1889, ii. 40, 481); Ling (Chem. Soc. Trans. 1892, 61, 559); Kollrepp (Annalen, 1886, 234, 14).

Heat of combustion at constant pressure, 580·4 cal. (Valeur, Ann. Chim. Phys. 1900, vii. 21, 491).

Treated with alcoholic ammonia, the chlorine atoms are replaced by amino-groups (Kehrmann and Tiesler). Compound with *m*-nitroaniline (Niemeyer); *chloroimine*, m.p. 67°–68° (Kollrepp); *monoxime*, decomposes at 140° (Kehrmann, Ber. 1888, 21, 3318).

Trichloro-*p*-benzoquinone $C_6HCl_3O_2$. 2 parts of phenol-*p*-sulphonic acid obtained by heating equal weights of phenol and sulphuric acid at 100° are dissolved in a hot solution of 4 parts of potassium chlorate and excess of hydrochloric acid added. After standing 24 hours, finish the reaction by blowing in steam, filter and wash with hot water, then cold alcohol. Suspend the mixture of tri- and tetra-chloroquinones so obtained in 10 parts of water and lead in sulphur dioxide for 10 minutes. When hot, the trichloroquinol remains dissolved, filter and oxidise with fuming nitric or chromic acid (Knapp and Schultz, Annalen, 1881, 210, 174; Graebe, *ibid.* 1868, 146, 9; 1891, 263, 28; Stenhouse, *ibid.* Spl., 1868, 6, 218). For other methods of preparation, reactions and derivatives, *see* Staedeler (*ibid.* 1849, 69, 618); Carstanjen (Ber. 1869, 2, 633); Schmitt and Andresen (J. pr. Chem. 1881, ii. 23, 436; 1881, ii. 24, 434; 1883, ii. 28, 422); MacPherson and Fischer (J. Amer. Chem. Soc. 1900, 22, 141); Niemeyer (Annalen, 1888, 228, 325); E. Léger (Compt. rend. 1908, 146, 694); Jacobson, Bartsch and Steinbreck (Annalen, 1909, 367, 304).

Large yellow leaflets, m.p. 165°–166°; molecular heat of combustion at constant pressure 548.8 cal. (Valeur, Ann. Chim. Phys. 1900, vii. 21, 496).

Tetrachloro-*p*-benzoquinone or **Chloranil** $C_6Cl_4O_2$, is frequently produced from aromatic compounds, *e.g.* by the action of chlorine on an alcoholic solution of chloroisatin (Erdmann, Annalen, 1843, 48, 309) or by the action of potassium chlorate and hydrochloric acid on aniline (Fritzsche, Bull. Sci. St. Petersb., 1843, I. 103), phenol (Hofmann, Annalen, 1844, 52, 57), quinic acid (Staedeler, *ibid.* 1849, 69, 326), salicylic and nitrosalicylic acids (Hofmann); dinitrosalicylic acid (Stenhouse, *ibid.* 1851, 78, 4), tyrosin (Staedeler, *ibid.* 1860, 116, 99); *m*-aminobenzoic acid (Erlenmeyer, Jahresb. 1861, 404). It is also obtained by the action of fuming nitric acid on pentachlorophenol (Merz and Weith, Ber. 1872, 5, 460) and on 1 : 2 : 4 : 5-tetrachlorobenzene, but not on its isomers (Beilstein and Kurbatow, Annalen, 1878, 192, 236). For other methods of preparation and purification, some involving separation from trichloroquinone, *see* Graebe (*ibid.* 1891, 263, 23), Andresen (J. pr. Chem. 1883, ii. 28, 425), Knapp and Schultz (Annalen, 1881, 210, 176), Stenhouse (*ibid.* Spl., 1868, 6, 209), Barral (Bull. Soc. chim. 1894, iii. 11, 708), Elbs and Brunnschweiler (J. pr. Chem. 1895, ii. 52, 560), Witt and Toeche-Mittler (Ber. 1903, 36, 4390), Bouveault (Ann. Chim. Phys. 1908, viii. 13, 142), Brazier and McCombie (Chem. Soc. Trans. 1912, 101, 968).

Originally, phenol was usually employed for the preparation of chloranil. Graebe found a purer product was obtained from *p*-phenylenediamine, the yield being also better, whilst Witt and Toeche-Mittler (*l.c.*) obtained the best results with 2 : 6-dichloro-*p*-phenylenediamine.

A lukewarm solution of 16·4 grms. of potassium chlorate is added gradually to a solution of 28 grms. of *p*-nitroaniline in 250 c.c. of concentrated hydrochloric acid at 50°. Much water is added and the precipitate collected. Yield of crude product, 36 grms. (87 p.c. of theory). Once recrystallised from glacial acetic acid or acetic acid and alcohol gives a dichloronitroaniline, melting at 185°–187°.

12 grms. of dichloronitroaniline in 300 c.c. of concentrated hydrochloric acid are reduced with 13 grms. of granulated tin; to the boiling hot solution 10 grms. of potassium chlorate crystals are added: 11 grms. of chloranil, m.p. 268°–270°, are obtained. One crystallisation from toluene raises the melting-point to 285°–286°. On a large scale, yields up to 90 p.c. of the theoretical were obtained.

Chloranil sublimes readily, m.p. (in sealed tube) 290°. Molecular heat of combustion at constant pressure, 519 cal. (Valeur, Ann. Chim. Phys. 1900, vii. 21, 499). Other properties and reactions, *see* Graebe (Annalen, 1868, 146, 12; 1891, 263, 19), Sarauw (*ibid.* 1881, 209, 125), Levy and Schultz (Ber. 1880, 13, 1430; Annalen, 1881, 210, 154), Knapp and Schultz (*ibid.* 1881, 210, 189), Niemeyer (*ibid.* 1888, 228, 326), Jackson and Torrey (Amer. Chem. J. 1898, 20, 427), Imbert and Pagès (Bull. Soc. chim. 1898, iii. 19, 575), Imbert (Compt. rend. 1901, 133, 162).

Technically, chloranil has been used for oxidising leucobases to dyestuffs (Meister, Lucius and Brüning, D. R. P. 11412, 1879). Heated with aromatic amines, dyestuffs are produced (Greiff, Ber. 1879, 12, 1610). At one time spirit soluble dyes, known as 'chloranil blue,' were prepared from chloranil and derivatives of diphenylamine. In 1879, Meister, Lucius and Brüning patented the production of violet, blue, or green dyes by heating dimethylaniline, methyldiphenylamine (or its homologues) and benzyldiphenylamine (or its homologues) respectively with chloranil. The chloranil behaved simply as an oxidising agent (D. R. P. 11811, lapsed 1882; compare also Ber. 1879, 12, 1952; 1883, 16, 2005, 2904, 3044; 1884, 17, 100).

Quinone-imide dyestuffs are obtained by condensing chloranil with amino-hydroxy-aromatic acids (von Heyden, D. R. P. 119863, 1898).

2-Bromo-*p*-benzoquinone $C_6H_3BrO_2$, m.p. 55°–56° (Sarauw, Annalen, 1881, 209, 106). *Oxime* (?), a mixture (Kehrmann, Ber. 1888, 21, 317). 2 : 4-*Dibromophenylimine*, m.p. 112° (Smith and Orton, Chem. Soc. Trans. 1908, 93, 318).

2 : 5-Dibromo-*p*-benzoquinone $C_3H_2Br_2O_2$, m.p. 188° (Benedikt, Monatsh. 1880, I, 346; Sarauw, Annalen, 1881, 209, 113).

2 : 6-**Dibromo-*p*-benzoquinone,** m.p. 131° (Levy and Schultz, Annalen, 1881, 210, 158; Henrichsen, *ibid.* 1889, 253, 286; Thiele and Eichwede, Ber. 1900, 33, 673; van Erp, Rec. trav. chim. 1911, 30, 270). *Hydroxyphenylimine* $C_6H_2Br_2O(:N.C_6H_4OH)$ (Möhlau, *ibid.* 1883, 16, 2845). *Diimine hydrobromide* (Jackson and Calhane, *ibid.* 1902, 35, 2495).

2 : 6-*Dibromo*-1 : 4-*dimethylthioniumquinone* $C_6H_2Br_2[:S(CH_3)]_2:O$, m.p. 251°–252°; by the action of alkali on $C_3H_2Br_2[S(CH_3)_2I]OH$ (Zincke and Glahn, Ber. 1907, 40, 3046).

2 : 6-*Dibromo-p-benzoquinone-4-oxime* blackens at 160°, explodes at 168°–175° (O. Fischer and Hepp, Ber. 1888, 21, 674; Kehrmann, *ibid.* 3318; Forster and Robertson, Chem. Soc. Trans. 1901, 79, 687; van Erp, *loc. cit.*): *acetyl derivative*, m.p. 122°; *benzoyl derivative*, m.p. 197°; 4-Chloroimine, m.p. 78° (Möhlau, Ber. 1883, 16, 2845; Friedländer and Stange, *ibid.* 1893, 26, 2262).

Two other dibromobenzoquinones melting at 76° (Böhmer, J. pr. Chem. 1881, ii. 24, 464) and 88° (Prunier, Ann. Chim. Phys. 1878, v. 15, 67) have been described.

Tribromo-*p*-benzoquinone, m.p. 147° (Sarauw, Annalen, 1881, 209, 120; Prunier, *l.c.*; Stenhouse, Annalen Spl., 1872, 8, 20; Heermann, Ber. 1877, 10, 110).

Tetrabromo-*p*-benzoquinone or **bromanil** $C_6Br_4O_2$, m.p. 300°. For preparation, *see* Stenhouse (Annalen, 1854, 91, 307; Spl., 1872, 8, 18); Sarauw (Annalen, 1881, 209, 126); Hübner (*ibid.* 1867, 143, 255); Hlasiwetz and Habermann (*ibid.* 1871, 159, 320); Schunck and Marchlewski (*ibid.* 1894, 278, 348); Graebe and Weltner (*ibid.* 1891, 263, 33); Losanitsch, Ber. 1882, 15, 374); Ling (Chem. Soc. Trans. 1892, 61, 568); Simonis and Wenzel (Ber. 1900, 33, 421); Auwers and Büttner (Annalen, 1898, 302, 133, 142). The method of Graebe and Weltner is to be recommended. Numerous chloro-bromo-quinones have been prepared.

2 : 5-**Diiodo-*p*-benzoquinone,** m.p. 157°–159° (Metzeler, Ber. 1888, 21, 2555).

2 : 6-**Diiodo-*p*-benzoquinone,** m.p. 178° (R. Seifert, J. pr. Chem. 1883, ii. 28, 438; Kehrmann and Messinger, Ber. 1893, 26, 2377; Kehrmann, J. pr. Chem. 1887, ii. 37, 336; Willgerodt and Arnold, Ber. 1901, 34, 3351). *Dibromodiiodo-*, *Bromotriiodo*, and *Tetraiodo-p-benzoquinones* melt at 258°–259°, 253°–254°, and 282°–284° respectively (Torrey and Hunter, J. Amer. Chem. Soc. 1912, 34, 702).

2-**Nitro-*p*-benzoquinone** $C_6H_3(NO_2)O_2$. The compound described by Friedländer (Ber. 1895, 28, 1387) is really 2-nitro- 3 or 6-*m*-nitro-*p*-hydroxyanilinequinone (Kehrmann and Idzkowska, Ber. 1899, 32, 1066). The 2 : 6-**dichloro-** and 2 : 6-**chlorobromo-derivatives** of **nitroquinone** have been described (Guareschi and Daccomo, *ibid.* 1885, 18, 1171; Garzino, Atti. R. Accad. Sci. Torino, 1890, 25, 250).

2 : 3-**Dicyano-*p*-benzoquinone** $C_6H_2(CN)_2O_2$. By oxidation of dicyanoquinol with the vapour of nitric acid (Thiele and Günther, Annalen, 1906, 349, 45).

The requisite dicyanoquinol is obtained by dissolving 2 kilos. of quinone in 60 litres of alcohol and 2·5 litres of concentrated sulphuric acid. A concentrated solution of potassium cyanide is added at ordinary temperature until the reaction is faintly alkaline: the solution shows a green fluorescence at this stage. The liquid is acidified, diluted with water and extracted with ether. The residue left after distilling off the ether is diluted with water and the dicyanoquinol precipitated as brownish leaflets. By recrystallising from water with addition of animal charcoal, feebly yellow coloured needles of the formula $C_6H_2(CN)_2(OH)_2+2H_2O$ are obtained (Bayer and Co., D. R. P. 117005, 1899; Thiele and Meisenheimer, Ber. 1900, 33, 675).

***p*-Benzoquinone-2-carboxylic acid** $C_6H_3(CO_2H)O_2$.

Nitrososalicylic acid is the 4-oxime. By adding acetic acid to a solution of potassium salicylate and sodium nitrite. Converted by ferric chloride to a green dyestuff (Bayer and Co., D. R. P. 48491, 1888). Also obtained by boiling 5-nitroso-N-methylanthranilic acid with aqueous sodium carbonate (Houben and Brassert, Ber. 1907, 40, 4739), m.p. 162°–163°. The *oxime-methylimine* $C_6H_3(:NOH)(:NCH_3)COOH$ has been obtained (Houben, Brassert and Ettinger, *ibid.* 1909, 42, 2745).

***p*-Benzoquinone-2 : 3-dicarboxylic acid** $C_6H_2(CO_2H)_2O_2$.

The anhydride and imide have been prepared (Thiele and Günther, Annalen, 1906, 349, 45).

2-**Amino-*p*-benzoquinone** $C_6H_3(NH_2)O_2$. The *acetyl derivative*, m.p. 142°, is obtained by the oxidation of 2 : 4- or 3 : 4-diacetaminophenol (Kehrmann, Bahatrian and Gauhe, Ber. 1898, 31, 2400, 2404). Salts of 2-*amino*-p-*benzoquinone-4-imine* have been obtained by the oxidation of 2 : 4-aminophenol (Kehrmann and Prager, *ibid.* 1906, 39, 3437). *Aminoquinone-diphenyldiimine* $C_6H_3(NH_2)(:N{\cdot}C_6H_5)_2$, m.p. 167°, results from the oxidation of neutral solutions of aniline salts by manganese or lead peroxide (Börnstein, *ibid.* 1901, 34, 1268). It yields azophenine on heating with aniline and its hydrochloride.

5-Chloro-2-acetaminobenzoquinone, m.p. 174°–175°.

5-Bromo-2-acetaminobenzoquinone, m.p. 183°–185°.

2-**Anilino-*p*-benzoquinone** $C_6H_3(NH{\cdot}C_6H_5)O_2$. By oxidation of anilino-quinol with N/10 ferric chloride (Willstätter and Majima, Ber. 1910, 43, 2588). The 4-phenylimine is obtained by adding sodium nitrite to 1-amino-2 : 4-dianilinobenzene in hydrochloric acid, m.p. 125° (O. Fischer and Heiler, *ibid.* 1893, 26, 385); 3 : 6- and 3 : 5-dichloro- and 3 : 5 : 6-trichloro-derivatives of anilinoquinone (Niemeyer, Annalen, 1885, 228, 332, 335, 337).

Many arylamino-quinones can be prepared by the general reaction

$$2C_6H_4O_2+NH_2R=C_6H_3(NHR)O_2+C_6H_4(OH)_2$$

(Liebermann and Jacobson, Annalen, 1883, 221, 75; Zincke, Ber. 1881, 14, 1494). If an aminophenolcarboxylic acid is used, mordant dyestuffs are obtained (von Heyden, D. R. P. 119863, 1898). Thus, for example, 19 kilos. of aminosalicylic acid are dissolved with 14 kilos. of sodium acetate in 300 kilos. of alcohol. A solution of 11 kilos. of benzoquinone in 300 kilos. of alcohol is added and the mixture boiled from 3 to 5 hours. Then 500 kilos. of alcohol are distilled off and 500 kilos. of water added to the residue. The precipitated colouring matter is repeatedly washed and made up as a paste or as sodium salt. The colouring matter gives a bright brown on wool, deep brown shades may be obtained on a chrome mordant which may be used before or after the dyeing operation.

In addition to benzoquinone, chloranil or β-naphthaquinone may be used; the acids employed are *o*- and *p*-aminosalicylic, *p*-amino-*m*-cresotinic, *p*-amino-*o*-cresolcarboxylic, amino-α-hydroxynaphthoic, amino-β-hydroxynaphthoic.

2 : 5-Diamino-*p*-benzoquinone $C_6H_2(NH_2)_2O_2$, decomposes at 325°–330°. It is obtained by hydrolysis of its *diacetyl derivative*, the oxidation product of 2 : 5-diacetaminophenol (Kehrmann and Betsch, Ber. 1897, 30, 2099). *6-Chloro-2 : 5-diacetaminoquinone*, m.p. 225°–226° (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 491). *Diimine* (Nietzki, Ber. 1887, 20, 2115).

Tetramethyl-2 : 5-diamino-*p*-benzoquinone

$$C_6H_2[N(CH_3)_2]_2O_2.$$

From quinone or chloroquinone and dimethylamine (Mylius, Ber. 1885, 18, 467: Kehrmann, *ibid.* 1890, 23, 905).

Diethyl-2 : 5-diglycinoquinone

$$C_6H_2(NH{\cdot}CH_2{\cdot}CO_2C_2H_5)_2,$$

m.p. 215°; *diethyl-2 : 5-dialaninoquinone*

$$C_6H_2[NH{\cdot}CH(CH_3){\cdot}CO_2C_2H_5]_2,$$

m.p. 140° (E. Fischer and Schrader, Ber. 1910, 43, 525).

2-Amino-5-anilino-*p*-benzoquinone

$$C_6H_2(NH_2)(NH{\cdot}C_6H_5)O_2,$$

m.p. 280°–282° (Kehrmann and Bahatrian, Ber. 1898, 31, 2401).

Phenylimine $C_6H_2(NH)(NH{\cdot}C_6H_5)(:N{\cdot}C_6H_5)O$ (Majima, *ibid.* 1911, 44, 229).

2 : 5-Dianilino-*p*-benzoquinone (*quinone-anilide*) $C_6H_2(NH{\cdot}C_6H_5)_2O_2$. From quinone and aniline (Hofmann, Jahresb. 1863, 415; Wichelhaus, Ber. 1872, 5, 851; Knapp and Schultz, Annalen, 1881, 210, 178) and by other reactions (Niemeyer, *ibid.* 1885, 228, 331; O. Fischer and Hepp, Ber. 1888, 21, 2618; Hebebrand and Zincke, *ibid.* 1883, 16, 1556; Willstätter and Majima, *ibid.* 1910, 43, 2588). The *monoimine* is obtained by oxidising aniline with sodium persulphate (Majima, *ibid.* 1911, 44, 229).

The *phenylimine* and the *diphenyldiimine* (*azophenine*) are of considerable interest as being intermediate compounds in the formation of indulines by heating hydroxy- and amino-azo-compounds with aniline.

2 : 5-Dianilino-*p*-benzoquinone-phenylimine

$$C_6H_2({\cdot}NHC_6H_5)_2(:N{\cdot}C_6H_5):O$$

is produced by heating 1 part of benzoquinone with 20 parts of glacial acetic acid and 2 parts of aniline (Zincke and Hagen, Ber. 1885, 18, 787); by long continued boiling of 2 parts of aniline with 1 part of *o*-nitrophenol and 10–20 parts of 50 p.c. acetic acid (O. Fischer and Hepp, Annalen, 1891, 262, 247); by heating *m*-hydroxydiphenylnitrosamine

$$HO{\cdot}C_6H_4{\cdot}N(NO){\cdot}C_6H_5$$

with aniline and its hydrochloride to 100° (Kohler, Ber. 1888, 21, 910; Fischer and Hepp, *ibid.* 675; Annalen, 1891, 262, 249); by warming quinone-phenylimine with 15–20 parts of aniline at 100° (Bandrowski, Monatsh. 1888, 9, 415); from 5-diazo-2-hydroxy-benzoic acid and aniline (Dierbach, Annalen, 1893, 273, 118); by warming aniline with hydrogen peroxide and dilute acetic acid (Schunck and Marchlewski, Ber. 1892, 25, 3574); by the action of haemin on aniline (Küster, *ibid.* 1910, 43, 2962); accompanied by amino-anilino-quinone-phenylimine by oxidising aniline in aqueous acetic acid solution at 0° with sodium bromate (Majima, *ibid.* 1911, 44, 229); by the electrolytic reduction of *p*-nitrophenol in a mixture of 2 parts of aniline and 1 part of hydrochloric acid (sp.gr. 1·19) (Löb, Zeitsch. Elektrochem. 1900, 6, 441); and by the action of aniline on *o*-benzoquinone (Jackson and Koch, Ber. 1898, 31, 1457). M.p. 203°. Yields ethers of anilinohydroxyquinone-phenylimine when heated with alcohols and sulphuric acid, and azophenine on continued heating with aniline at 180°–200°.

2 : 5-Dianilino-*p*-benzoquinone-diphenyldiimine (*azophenine*) $C_6H_2(NH{\cdot}C_6H_5)_2(:N{\cdot}C_6H_5)_2$ is obtained by heating *p*-nitrosophenol with aniline salts (Kimich, Ber. 1875, 8, 1028; Witt and Thomas, Chem. Soc. Trans. 1883, 43, 115); by heating 2 parts of aminoazobenzene with 4 parts of aniline and 1 part of aniline hydrochloride for 24 hours to 80°–90° (Witt and Thomas; also Witt, Ber. 1887, 20, 1539), and by numerous other reactions (Witt, *ibid.* 1877, 10, 1311; O. Fischer and Hepp, *ibid.* 1887, 20, 2480; 1888, 21, 683, 686; Annalen, 1889, 255, 146; 1890, 256, 258; Ikuta, *ibid.* 1888, 243, 285; Szarvasy, Chem. Soc. Trans. 1900, 77, 207; Börnstein, Ber. 1901, 34, 1268).

For the preparation of the substance, Fischer and Hepp recommend heating 100 grms. of nitrosodiphenylamine with 500 grms. of aniline and 100 grms. of aniline hydrochloride for 8–10 hours on the water-bath. The crystals which separate are washed successively with water, dilute alcohol and absolute alcohol and then recrystallised from toluene; m.p. 246°. Soluble in chloroform: the solution in concentrated sulphuric acid is violet and suddenly turns blue at 100°. Heated to 360°, azophenine yields aniline and fluorindine; heated with primary bases, indulines are produced. Water-soluble indulines are produced when *p*-phenylenediamine is employed (Dahl and Co., D. R. P. 43008, 1887), whilst bluish-grey water-soluble dyestuffs are formed by heating with hydrochlorides of nitrosodialkylanilines in glacial acetic acid solution (Farbw. Griesheim, D. R. P. 55229, 1890). By long continued boiling with alcohol and sulphuric acid, aniline and dianilinoquinone are produced. Reduction gives tetra-anilinobenzene (hydrazophenine), m.p. 173°–174° (Fischer and Hepp, Ber. 1887, 20, 2483). Several halogen derivatives have been prepared (Fischer and Hepp, Ikuta).

Methylazophenine $C_{31}H_{26}N_4$, from *p*-nitrosophenyltolylamine and aniline, melts at 230° (Reichold, Annalen, 1889, 255, 166).

2 : 5-Di-methylphenylamino-*p*-benzoqiunone

$$C_6H_2[N(CH_3)(C_6H_5)]_2O_2.$$

By warming an alcoholic solution of monomethylaniline with quinone. Red-brown leaflets with blue reflex (Möhlau and Redlich, Ber. 1911, 44, 3616).

Dianilino - chloro - *p* - benzoquinone. The phenylimine, $C_6HCl(NHC_6H_5)_2(:NC_6H_5):O$, m.p. 195°, is obtained by adding 5 molecular proportions of aniline to an alcoholic solution of trichloroquinone-chloroimine (Andresen, J. pr. Chem. 1883, ii. 28, 428).

3 : 6-Dichloro-2 : 5-diamino-*p*-benzoquinone (*chloranilimide*) $C_6Cl_2(NH_2)_2O_2$ is obtained by the action of ammonia on chloranil (Laurent, Ber. Jahresbericht, 25, 850; Knapp and Schultz, Annalen, 1881, 210, 184), or on the dimethyl ether of chloranilic acid (Kehrmann, J. pr. Chem. 1889, ii. 40, 371). Fine reddish-brown needles; sublimes. Insoluble in water, alcohol, ether and ammonia; dissolves in alcoholic potash with a violet-red colour and on boiling with caustic potash solution gives ammonia and chloranilic acid.

3 : 6-Dichloro-2 : 5-dianilino-*p*-benzoquinone (*chloranilanilide*) $C_6Cl_2(NHC_6H_5)_2O_2$, results from the action of aniline on chloranil (Hesse, Annalen, 1860, 114, 306; Hofmann, Jahresb. 1863, 415; Knapp and Schultz, Annalen, 1881, 210, 187), and by other reactions (Schmitt and Andresen, J. pr. Chem. 1881, ii. 24, 431; Andresen, *ibid.* 1883, ii. 28, 427; Niemeyer, Annalen, 1885, 228, 333). Yellowish-brown metallic tablets, m.p. 285°–290°, sublimes with very little decomposition. The *diphenylimine* (*dichloroazophenine*) has been described by Bandrowski and Prokopeczko (Bull. Acad. Sci. Cracow, 1901, 441).

Other derivatives of quinone containing groups $\cdot NHR$ and $\cdot NR_2$ in positions 2 and 5 are described by Schmitt and Andresen; Ville and Astre (Bull. Soc. chim. 1895, iii. 13, 746; 1896, iii. 15, 1027, 1033); Jackson and Torrey (Ber. 1897, 30, 531; Amer. Chem. J. 1898, 20, 419); Imbert and Pagès (Bull. Soc. chim. 1898, iii. 19, 575).

3 : 6-Dinitro-2 : 5-diamino-*p*-benzoquinone

$C_6(NO_2)_2(NH_2)_2O_2$

is obtained by adding the nitrate of diaminoquinone-diimine to 15–20 parts of concentrated sulphuric acid at a temperature below 10°. Dark yellow needles, gives tetraaminoquinol on reduction (Nietzki, Ber. 1887, 20, 2115).

3-Nitro-2 : 5-dianilino-*p*-benzoquinone

$C_6H(NO_2)(NHC_6H_5)_2O_2$

(Kehrmann and Idzkowska, Ber. 1899, 32, 1067).

2 : 6-Diamino-*p*-benzoquinone $C_6H_2(NH_2)_2O_2$ and the hydrochloride of its 4-*imine* are obtained by the oxidation of 1 : 2 : 3 : 5-tetraaminobenzene with ferric chloride (Nietzki and Hagenbach, Ber. 1897, 30, 542). The *diacetyl-derivative*, m.p. 265°–270°, by oxidising triacetaminophenol (Bamberger, Ber. 1883, 16, 2402) or tetraacetyldiaminoquinol (Nietzki and Preusser, *ibid.* 1886, 19, 2247; 1896, 29, 797). *Diphthalyl derivative*, m.p. 277° (Piutti, Gazz. chim. ital. 1886, 16, 254).

Triamino-*p*-benzoquinone $C_6H(NH_2)_3O_2$. By drawing air through a solution of pentaaminobenzene hydrochloride (1 grm.) and sodium acetate (2 grms.) in water (150 c.c.) for 2 days. Dark brown, insoluble, easily decomposable powder (Jackson and Grindley, Ber. 1893, 26, 2305).

Hydroxyquinones. The hydroxyquinones are of considerable theoretical interest and in the naphthalene and anthracene series acquire considerable importance as dyestuffs.

2-Hydroxy-*p*-benzoquinone $C_6H_3(OH)O_2$. By oxidising 1 : 2 : 4-trihydroxybenzene in absolute ethereal solution with silver oxide. Crystallises in yellow rectangular tablets. Turns brown at 120°, black at 124°, but does not melt. Liberates iodine from hydriodic acid, easily reduced to trihydroxybenzene with which a quinhydrone can be obtained (R. Willstätter and F. Müller, Ber. 1911, 44, 2181).

Compounds of apparently the same empirical formula have been described as 'melanic' acids. They result by boiling tannin with caustic potash or by oxidising solutions of salicylaldehyde or quinone (Büchner, Annalen, 1845, 53, 373; Piria, *ibid.* 1841, 39, 167; Woskresensky, J. pr. Chem. 1845, 34, 251).

Nitrosoresorcinol (Fèvre, Bull. Soc. chim. 1883, 39, 585) and dinitrosoresorcinol (Fitz, Ber. 1875, 8, 631) can, in the tautomeric forms

$C_6H_3(OH)(:NOH):O$ and

$C_6H_2(NO)(OH)(:NOH):O$,

be regarded as the *monoximes* of *hydroxyquinone* and *nitrosohydroxyquinone* respectively (*see* also Kostanecki, Ber. 1887, 20, 3133).

Mononitrosoresorcinol has been used in the preparation of oxazine dyestuffs (resorcin blue), which proved to be of little technical value (Bindschedler and Busch, D. R. P. 14622, 1880).

Dinitrosoresorcinol is used as a paste under the names of 'fast green' and 'solid green' on silk or cotton mordanted with iron. A method for directly colouring the fibre with lakes of quinone-oximes is to impregnate the material with a phenol (*e.g.* resorcinol), a mordant (ferrous, chromium or cobalt salt) and an acid, then to dry and subsequently pass the goods through a boiling neutral nitrite solution (Kalle and Co., D. R. P. 99486, 1897; 101523, 1898).

Dinitrosoresorcinol gives a fast brown dyestuff, *essacine*, when acted on by sodium hyposulphite ($NaHSO_2$) (Kendall, D. R. P. 54615). A different colouring matter is produced when it is reduced with sodium hydrogen sulphite (Binder, D. R. P. 65049, 1891).

A derivative of hydroxyquinone is *chrysone* $C_{15}H_8O_5$, obtained by oxidation of chrysin. Gives colour reactions of anthocyanin (M. Nierenstein, Ber. 1912, 45, 499).

2-Methoxy-*p*-benzoquinone $C_6H_3(OCH_3)O_2$. By oxidation of *o*-anisidine (Mühlhäuser, Annalen, 1881, 207, 251; Will, Ber. 1888, 21, 605); the dimethyl ether of *p*-aminoresorcinol (Bechhold, Ber. 1889, 22, 2381); or 3-methoxy-4-aminophenol (Henrich and Rhodius, *ibid.* 1902, 35, 1486), m.p. 140°. *Monoxime* (nitrosoguiacol) several derivatives (Bridge and Morgan, Amer. Chem. J. 1899, 22, 486). *Dioxime*, m.p. 250° (Best, Annalen, 1889, 255, 187; Pfob, Monatsh. 1897, 18, 473).

2-Ethoxy-*p*-benzoquinone $C_6H_3(OC_2H_5)O_2$, m.p. 117° (Will and Pukall, Ber. 1887, 20, 1132; Kietaibl, Monatsh. 1898, 19, 552).

Trichlorohydroxy-*p*-benzoquinone

$C_6Cl_3(OH)O_2$,

m.p. 194°, yields chloranilic acid when warmed with alkalis (Zincke and Schaum, Ber. 1894, 27, 556).

Tribromohydroxy-*p*-benzoquinone

$C_6Br_3(OH)O_2$,

m.p. 205°. By hydrolysis of the hemiacetal $C_6Br_3(OH)O(OCH_3)_2$ (Jackson and Flint, Amer. Chem. J. 1908, 39, 80). The 'tribromoxyhydrochinon,' m.p. 206°–207°, obtained by the action of bromine on 1 : 2 : 4-trihydroxybenzene is probably identical (Barth and Schreder, Monatsh. 1884, 5, 593).

5-Amino-2-hydroxy-*p*-benzoquinone

$$C_6H_2(NH_2)(OH)O_2.$$

The *monoimine* is identical with diiminoresorcin; *acetyl derivative* $C_6H_2(NHCOCH_3)(OH)O_2$, m.p. 170° (Nietzki and Schmidt, Ber. 1889, 22, 1657; Kehrmann and Betsch, *ibid.* 1897, 30, 2102).

5-Dimethylamino-2-hydroxy-*p*-benzoquinone $C_6H_2[N(CH_3)_2][OH]O_2$. Red crystals (Kehrmann, Ber. 1890, 23, 906).

5-Anilino-2-hydroxy-*p*-benzoquinone

$$C_6H_2(NHC_6H_5)(OH)O_2$$

and several derivatives (Zincke and Hagen, Ber. 1885, 18, 788). Melts and decomposes at 228°–230° (Kehrmann and Bahatrian, *ibid.* 1898, 31, 2401).

For other derivatives of 5-amino-2-hydroxyquinone, *see* Fischer and Hepp (Ber. 1888, 21, 677); Kehrmann (*ibid.* 1890, 23, 900); Jackson and Torrey (*ibid.* 1897, 30, 529; Amer. Chem. J. 1898, 20, 410). Ethers of the type

$$C_6Cl(OC_2H_5)(NRR')_2O_2$$

have been prepared by Kehrmann (J. pr. Chem. 1891, ii. 43, 261).

2 : 5-Dihydroxy-*p*-benzoquinone

$$C_6H_2(OH)_2O_2$$

is obtained by elimination of carbon dioxide from dihydroxyquinonedicarboxylic acid

$$C_6(OH)_2(CO_2H)_2O_2,$$

and by oxidation of 1 : 2 : 4 : 5-tetrahydroxybenzene with ferric chloride (Löwy, Ber. 1886, 19, 2387). Also by heating diiminoresorcinol with 10 parts of 10 p.c. caustic potash at 70° (Nietzki and Schmidt, *ibid.* 1888, 21, 2374; 1889, 22, 1654) and by heating anilinohydroxyquinone or its anilide or tetramethyldiaminoquinone with dilute alkalis. It can be obtained from dianilino-quinone or chloro-dianilinoquinone by heating with a mixture of 3 parts of concentrated sulphuric acid and 2 parts of alcohol (Kehrmann, Ber. 1890, 903); together with methyl-*o*-aminophenol by heating N-methylphenoxazine-*o*-quinone with sodium hydroxide solution (Diepolder, *ibid.* 1899, 32, 3523); by heating 2-amino-5-anilinoquinone with caustic soda or dilute sulphuric acid (Kehrmann and Bahatrian, *ibid.* 1898, 31, 2402) and by alkaline hydrolysis of the diethyl ether (Knoevenagel and Bückel, *ibid.* 1901, 34, 2402). Melts and partially decomposes at 215°–220°.

Strong acid giving highly coloured salts; stannous chloride reduces to tetrahydroxybenzene. Bromine and caustic soda give bromanilic acid; nitric acid gives nitranilic acid. The compound $C_6H_6O_4N_2$ obtained with hydroxylamine and formulated by Nietzki and Schmidt (Ber. 1888, 21, 2377) as a dioxime, is really hydroxylaminohydroxyquinone-monoxime as it gives 4 : 6-diaminoresorcinol on reduction (Kehrmann and Betsch, *ibid.* 1897, 30, 2097). Reacts tautomerically as 4 : 5-dihydroxy-*o*-quinone, with *o*-phenylenediamine, dihydrophenazine is produced. 2 : 5-Dihydroxy-quinone apparently gives two series of ethers,

$$C_6H_2(OAlkyl)_2O_2.$$

Dimethyl ethers (Hofmann, Ber. 1878, 11, 332; Will, *ibid.* 1888, 21, 608; Nietzki and Schmidt, *ibid.* 2376; Nietzki and Rechberg, *ibid.* 1890, 23, 1216; Ciamician and Silber, *ibid.* 1893, 26, 786; Knoevenagel and Bückel, *ibid.* 1901, 34, 3996). *Diethyl ethers* (Nietzki and Rechberg, Knoevenagel and Bückel). *Dipropyl ether*, m.p. 187°, and *dibenzoyl derivative*, m.p. 174° (Knoevenagel and Bückel).

6-Chloro-2 : 5-dihydroxy-*p*-benzoquinone

$$C_6HCl(OH)_2O_2$$

melts and decomposes at 240° (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 484).

6-Chloro-2 : 5-diphenoxy-*p*-benzoquinone

$$C_6HCl(OC_6H_5)_2O_2,$$

m.p. 169°–170° (Jackson and Grindley, Amer. Chem. J. 1895, 17, 655).

3 : 6-Dichloro-2 : 5-dihydroxy-*p*-benzoquinone (*chloranilic acid*) $C_6Cl_2(OH)_2O_2+2H_2O$. By the action of potassium hydroxide on chloranil (Erdmann, Annalen, 1843, 48, 315) or trichloroquinone (Graebe, *ibid.* 1868, 146, 24)

$$C_6Cl_4O_2+4KOH=C_6Cl_2(OK)_2O_2+2KCl+2H_2O.$$

$$2C_6HCl_3O_2+3KOH$$
$$=C_6Cl_2(OK)_2O_2+KCl+C_6HCl_3(OH)_2+H_2O$$

Preparation. 10 parts of chloranil are moistened with alcohol and added to a solution of 9 grms. of sodium hydroxide in 210 grms. of water at 70°–80°. After 2 hours, 20 grms. of sodium chloride are added, the sodium chloranilate is washed with 10 p.c. brine, dissolved in boiling water and precipitated with hydrochloric acid (Stenhouse, Annalen Spl., 1872, 8, 14; Graebe, Annalen, 1891, 263, 24). Loses water of crystallisation at 115°; melts in sealed tube at 283°–284° (Michael, Ber. 1895, 28, 1631). 100 parts water dissolve 0·19 acid at 13·5°, 1·4 parts at 99°. Solutions are violet-red. Strong acid; electric conductivity, Barth (*ibid.* 1892, 25, 837); Coffetti (Gazz. chim. ital. 1900, 30, ii. 238); Fiorini (*ibid.* 1901, 31, i. 35). Armstrong has suggested that the chloroanilates are derived from 4 : 5-dihydroxy-1 : 2-benzoquinone (Chem. Soc. Proc. 1893, 9, 57). Molecular heat of combustion at constant pressure, 486·2 cal. (Valeur, Ann. Chim. Phys. 1903, vii. 29, 507). Several reactions lead to compounds of the aliphatic series, *e.g.* nitric acid gives chlorpicrin and oxalic acid; iodine in alkaline solution gives iodoform (Jackson and Torrey, Amer. Chem. J. 1898, 20, 429).

The salts of the alkali metals dissolve in water with intense violet colour; most of the other salts are coloured precipitates (Hesse, Annalen, 1860, 114, 304; Stenhouse; Graebe; Erdmann; Pope (Chem. Soc. Trans. 1892, 61, 585); Jackson and Torrey).

a-Dimethyl ether $C_6Cl_2(OCH_3)_2O_2$, m.p. 141°–142°. From silver chloranilate and methyl iodide. This compound and an isomer, m.p. 157°–158° (*β-dimethyl ether*) are obtained by the action of methyl alcoholic potash on chloranil in the cold. The *a*-dimethyl ether unites directly with sodium methoxide, giving the sodium salt of *dichlorodimethoxy-quinone-dimethylhemiacetal* $(CH_3O)_2C_6Cl_2(OH)_2(OCH_3)_2$ (Jackson and Grindley, Amer. Chem. J. 1895, 17, 600). Several derivatives have been prepared (Jackson and Oenslager and Torrey, *ibid.* 1896, 18, 7; 1898, 20, 429).

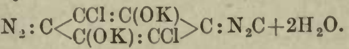
a-Diethyl ether, m.p. 104°–105°; *β-diethyl ether*, m.p. 97°–98° (Stenhouse; Kehrmann, J. pr. Chem. 1889, ii. 39, 318; 1889, ii. 40, 367; Jackson and Torrey).

Dibenzyl ether, m.p. 142° (Jackson and Oenslager).

Diphenyl ether, m.p. 243° (Jackson and Grindley).

Diacetyl derivative $C_6Cl_2(OCOCH_3)_2O_2$, m.p. 182·5° (Nep, J. pr. Chem. 1890, ii. 42, 170).

Biscyanimide



$$CN_2:C<\begin{matrix}CCl:C(OK)\\C(OK):CCl\end{matrix}>C:N_2C+2H_2O.$$

Form potash and cyanamide on chloranil in boiling aqueous suspension (Imbert, Compt rend. 1898, 126, 1879).

3 : 6-Dichloro-2-amino-5-hydroxy-*p*-benzoquinone $C_6Cl_2(NH_2)(OH)O_2$, obtained as ammonium salt by solution of chloranil in dilute aqueous ammonia (Erdmann, Annalen, 1843, 48, 321; Laurent, Ber. Jahresbericht, 25, 849).

3 : 6-Dibromo-2 : 5-dihydroxy-*p*-benzoquinone (*bromanilic acid*) $C_6Br_2(OH)_2O_2$. Preparation and properties resemble those of chloranilic acid (Stenhouse, Annalen, 1854, 91, 311; Sarauw, *ibid.* 1881, 209, 115; Hantzsch, Ber. 1887, 20, 1303; Salzmann, *ibid.* 1997; Hantzsch and Schniter, *ibid.* 2040; *ibid.* 1888, 21, 2438; Graebe and Weltner, Annalen, 1891, 263, 35; Levy and Jedlicka, *ibid.* 1889, 249, 81; Landolt, Ber. 1892, 25, 852; Ling, Chem. Soc. Trans. 1892, 61, 574; Pope, *ibid.* 586; Coffetti, Gazz. chim. ital. 1900, 30, ii. 238; Fiorini, *ibid.* 1901, 31, i. 35; Descomps, Bull. Soc. chim. 1899, iii. 21, 368). *Diethyl ether* $C_6Br_2(OC_2H_5)_2O_2$, m.p. 139° (Bentley, Amer. Chem. J. 1898, 20, 479). *Dimethylhemiacetal* of *dimethyl ether*

$$(CH_3O)_2C_6Br_2(OH)_2(OCH_3)_2,$$

m.p. 178°–188° (Jackson and Grindley, *ibid.* 1895, 17, 652). *Diphenyl ether* $C_6Br_2(OC_6H_5)_2O_2$, m.p. 266°–267° (Jackson and Grindley).

Biscyanimide $CN_2:C_6Br_2(OK)_2:N_2C$ (Imbert, Compt. rend. 1898, 126, 529).

3 : 6-Dibromo-2 : 5-diamino-*p*-benzoquinone (*bromanilamide*), from bromanil and alcoholic ammonia (Stenhouse).

3 : 6-Dibromo-2 : 5-dianilino-*p*-benzoquinone (Stenhouse, Annalen, 1872, Spl. 8, 22; van Erp, Rec. trav. chim. 1911, 30, 270).

3 : 6-Dibromo-2-amino-5-hydroxy-*p*-benzoquinone $C_6Br_2(NH_2)(OH)O_2$, from bromanil and aqueous ammonia (Stenhouse, *ibid.* 1854, 91, 313).

3-Chloro-6-bromo-2 : 5-dihydroxy *p*-benzoquinone $C_6ClBr(OH)_2O_2+H_2O$ (Levy, Ber. 1885, 18, 2370; Levy and Schultz, Annalen, 1881, 210, 163; Ling, Chem. Soc. Trans. 1887, 51, 785; Hantzsch, Ber. 1889, 22, 2829; Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 486; Pope, Chem. Soc. Trans. 1892, 61, 584; Ling and Baker, *ibid.* 591).

3-Chloro-6-iodo-2 : 5-dihydroxy-*p*-benzoquinone $C_6ClI(OH)_2O_2$. Explodes at 275°. Prepared by adding the theoretical amount of iodine dissolved in sodium hydroxide to an acidified solution of 6-chloro-2 : 5-dihydroxyquinone (Kehrmann and Tiesler, J. pr. Chem. 1889, ii. 40, 487).

3 : 6-Dicyano-2 : 5-dihydroxy-*p*-benzoquinone (*cyanilic acid*). The potassium salt, $C_8O_4N_2K_2$, is obtained by the reaction of chloranil and potassium cyanide in methyl alcohol solution. Strong acid, stable towards reducing and hydrolytic agents. The salts are fluorescent (M. M. Richter, Ber. 1911, 44, 3469).

3-Nitro-2 : 5-dihydroxy-*p*-benzoquinone

$$C_6H(NO_2)(OH)_2O_2.$$

By warming nitrodiiminoresorcinol with 10–15 parts of 10 p.c. solution of potassium hydroxide (Nietzki and Schmidt, Ber. 1889, 22, 1661). Golden yellow needles. For reactions compare also Kehrmann and Idzkowska (*ibid.* 1899, 32, 1071).

3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone (*nitranilic acid*) $C_6(NO_2)_2(OH)_2O_2$. By leading nitrous fumes into a well-cooled ethereal solution of quinol, a few drops of water being added towards the end of the reaction (Nietzki, Annalen, 1882, 215, 138); by the action of fuming nitric acid on quinol-dicarboxylic acid (Herrmann, *ibid.* 1882, 211, 342); by the action of nitric acid (generally mixed either with acetic or sulphuric acid) on dinitroquinol (Nietzki); quinol diacetate (Nietzki and Benckisser, Ber. 1885, 18, 499; *cf.* Nietzki, *ibid.* 1883, 16, 2093); dihydroxyquinonedicarboxylic acid (Hantzsch, *ibid.* 1886, 19, 2399), and on the triacetyl- and nitro- derivatives of 1 : 2 : 4-trihydroxybenzene (Thiele and Jäger, *ibid.* 1901, 34, 2838). It is also obtained by warming dinitro-diaminoquinone with dilute alkali (Nietzki and Benckisser, *ibid.* 1887, 20, 2116), and by the action of concentrated solution of sodium nitrite on chloranil (Nef, *ibid.* 1887, 20, 2028; Amer. Chem. J. 1889, 11, 17).

For the preparation of nitranilic acid, Nietzki and Benckisser recommend the solution of quinol diacetate in 6 parts of nitric acid (sp.gr. 1·48–1·50) at 10°, then cooling to −8° and adding 6 parts of concentrated sulphuric acid previously cooled to the same temperature. After standing some hours at −3° to 0°, the mixture is poured on to 12 to 15 parts of crushed ice, rapidly filtered and dissolved in potassium hydroxide solution. The potassium salt separates, is collected after 12 hours and recrystallised from hot water containing caustic potash. Nietzki (Ber. 1910, 43, 3457) states that potassium nitranilate is obtained in 75–80 p.c. yield by making a paste of quinol, acetic anhydride and a few drops of concentrated sulphuric acid and adding this to cold nitric acid (sp.gr. 1·48). Concentrated sulphuric acid is then poured in, the mixture is kept at 0° for 12 hours, poured on to ice and the solid product treated with ice and caustic potash (*see* also Henle, Annalen, 1906, 350, 334).

Nitranilic acid melts in its water of crystallisation, the anhydrous acid explodes at 170° without previous fusion. It is a strong acid, salts (Nef, Ber. 1887, 20, 2028; also Muthmann, *ibid.*). Electrical conductivity (Barth, Ber. 1892, 25, 837; Coffetti, Gazz. chim. ital. 1900, 30, ii. 237).

A compound $C_{12}H_6O_{10}N_2$ obtained by the action of nitrous acid on an ethereal solution of quinone has been formulated as an addition-product of quinone and nitranilic acid (J. Schmidt, Ber. 1900, 33, 3249).

Diamino-dihydroxy-*p*-benzoquinone

$$C_6(NH_2)_2(OH)_2O_2.$$

By oxidation of diaminotetrahydroxybenzene. Red brown needles; gives tetrahydroxyquinone when boiled with hydrochloric acid (Nietzki and Schmidt, Ber. 1885, 18, 1850).

Chloro-anilino-hydroxyethoxy-*p*-benzoquinone $C_6Cl(NHC_6H_5)(OH)(OC_2H_5)O_2$, m.p. 180° (Kehrmann, J. pr. Chem. 1891, ii. 43, 266).

Nitro-amino-dihydroxy-*p*-benzoquinone

$$C_6(NO_2)(NH_2)(OH)_2O_2.$$

By oxidising nitroaminotetrahydroxybenzene (Nietzki and Benckisser, Ber. 1885, 18, 500).

Chlorodihydroxy-*p*-benzoquinone-sulphonic acid $C_6Cl(OH)_2(SO_3H)O_2$. The salt

$$C_6Cl(OH)_2(SO_3K)O_2+2H_2O$$

(red needles) is obtained from the potassium salt of trichloroquinolsulphonic acid (Graebe, Annalen. 1868, 146, 55).

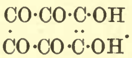
Dihydroxy-*p*-benzoquinone-disulphonic acid $C_6(OH)_2(SO_3H)_2O_2$, also known as euthiocronic acid, is obtained from thiocronic acid, the product of the action of potassium hydrogen sulphite on chloranil (Hesse, Annalen, 1860, 114, 318; Greiff, Jahresb. 1863, 392; Graebe, Annalen, 1868, 146, 46).

Trihydroxy-*p*-benzoquinone $C_6H(OH)_3O_2$, its *triacetyl-*, *tribenzoyl-* and *monobromo- derivatives* have been described (Merz and Zetter, Ber. 1879, 12, 2040).

6-**Chloro**-3-**ethoxy**-2:5-**dihydroxy**-*p*-**benzoquinone** $C_6Cl(OC_2H_5)(OH)_2O_2$, m.p. 168°–170° (Kehrmann, J. pr. Chem. 1891, ii. 43, 265).

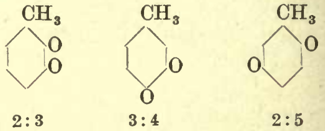
Tetrahydroxy-*p*-benzoquinone $C_6(OH)_4O_2$ results on exposing an aqueous solution of hexahydroxybenzene to the air (Lerch, Annalen, 1862, 124, 28), the sodium salt separates when air is passed for not too long a period through a solution containing hexahydroxybenzene and sodium carbonate (Nietzki and Benckisser, Ber. 1885, 18, 507, 1837). It is also formed when inosite is boiled with 4 to 5 parts of concentrated nitric acid (Maquenne, Ann. Chim. Phys. 1887, vi. 12, 112). Blue-black crystals, strong dibasic acid giving coloured salts; heated with acetyl chloride and zinc gives hexacetoxybenzene; nitric acid oxidises it to triquinoyl. *Diacetyl derivative*, m.p. 205° (Nietzki and Kehrmann, Ber. 1887, 20, 3152); *tetrabenzoyl derivative* (N. and K.; Maquenne, *l.c.*); phenylimine (Nietzki and Schmidt, Ber. 1888, 21, 1854). For *ethers* and *thio-ethers*, *see* Jackson and Grindley (Amer. Chem. J. 1895, 17, 579, 633) and Grindley and Sammis (*ibid.* 1897, 19, 290).

Benzene-diquinone $C_6O_4H_2$ is unknown: its dihydroxy-derivative is

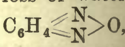
Rhodizonic acid 
$$\begin{matrix}CO\cdot CO\cdot C\cdot OH\\ \vdots \qquad\quad \vdots\\ CO\cdot CO\cdot C\cdot OH\end{matrix}.$$
Rhodizonic acid was first obtained from the black mass obtained in Brunner's method for the manufacture of potassium, the salt $C_6(OK)_6$ is contained therein (Heller, Annalen, 1837, 24, 1; 1840, 34, 232; 1862, 124, 32; Will, *ibid.* 1861, 118, 189). Also produced from triquinoyl by warming with sulphurous acid to 40°–50°; the salt $C_6O_6Na_2$ separates on saturation with sodium carbonate (Nietzki and Benckisser, Ber. 1885, 18, 513). Rhodizonic acid in the free state is colourless, crystalline and very unstable, oxidised by chlorine or dilute nitric acid to leuconic acid ($C_5H_8O_9$ or $C_5O_5,4H_2O$); a solution with sodium carbonate evaporated in the air gives croconic acid. The alkaline salts give intense reddish-yellow solutions which turn yellow on adding excess of alkali owing to the formation of salts of hydrocroconic acid. Astre has prepared salts $K_2C_6O_6$ and KHC_6O_6 from quinone and quinol by oxidation of alkaline solutions with air (Bull. Soc. chim. 1896, iii. 15, 460).

Benzene-triquinone or **triquinoyl** $C_6O_6,8H_2O$ has been obtained by acting on hexahydroxybenzene, tetrahydroxyquinone and rhodizonic acid with chlorine or nitric acid (Lerch, Annalen, 1862, 124, 34), and by the action of moderately concentrated nitric acid on 1:4-diaminotetrahydroxybenzene, diiminodihydroxyquinone or hexahydroxybenzene. Nietzki and Benckisser (Ber. 1885, 18, 504, 1842; *see* also Nietzki and Schmidt, *ibid.* 1888, 21, 1854) recommend the use of the above diamino- compound which is obtained by the reduction of nitranilic acid. Triquinoyl forms microscopic needles, melts about 95°, giving off carbon dioxide, insoluble in cold water, alcohol and ether. Liberates iodine from hydriodic acid, reduced by sulphurous acid to rhodizonic acid and by acid solution of stannous chloride to hexahydroxybenzene.

Toluquinones $C_7H_6O_2$. All three (two ortho and one para) toluquinones have been obtained; they will be referred to as



2:3-toluquinone, &c. Obtained by oxidation of dihydric phenols $C_6H_3(CH_3)(OH)_2$.

2:3-**Toluquinone.** Dark red prisms and needles, polymerises in ethereal solution to a bimolecular form, m.p. 194°–195° (Willstätter and F. Müller, Ber. 1911, 44, 2178). *Dioxime* $C_6H_3(CH_3)(:NOH)_2$, m.p. 140°; loss of water gives 1:2:3-toluylenefurazan,  $C_6H_4\!\!<\!\!\begin{smallmatrix}N\\N\end{smallmatrix}\!\!>\!O$, m.p. 44° (Zincke and Schwarz, Annalen, 1899, 307, 46).

5-**Amino**-2:3-**toluquinone** $C_6H_2(CH_3)(NH_2)O_2$ The hydrochloride of the 3-*imine*

$$C_6H_2(CH_3)(NH_2)(:NH,HCl):O$$

is obtained by adding excess of ferric chloride to a solution of diaminocresol dihydrochloride, saturated with sodium chloride. The dark red salt separates out at ordinary temperatures (Piccard, Ber. 1909, 42, 4332).

3:4-**Toluquinone.** From homocatechol in ethereal solution with silver oxide. Usually separates on rapidly evaporating the solvent as yellow mixed crystals, m.p. 65°–67°; on recrystallisation the dark red form, m.p. 80°–84°, is obtained. More stable than *o*-benzoquinone; polymerises to $(C_7H_6O_2)_2$. m.p. 124°–125° (Willstätter and F. Müller, Ber. 1911, 44, 2175; MacPherson and Boord, J. Amer. Chem. Soc. 1911, 33, 1525).

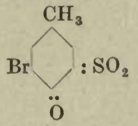
Dioxime, m.p. 127°–128°; 1:3:4-*toluylene-furazane*, m.p. 37° (Zincke and Schwarz, Annalen, 1899, 307, 43).

2:5:6-**Trichloro**-3:4-**toluquinone**

$$C_6(CH_3)Cl_3O_2,$$

m.p. 97°–98° (Cousin, Ann. Chim. Phys. 1898, [vii.] 13, 532) or 103° (Bergmann and Francke, Annalen, 1897, 296, 163).

5-Bromo-3 : 4-toluquinone. A quino-sulphone of the constitution



has been obtained in polymeric (colourless) form by abstracting the elements of hydrogen chloride from the sulphochloride

$C_6H_2Br(CH_3)(OH)(SO_2Cl)$

(Zincke and Kempf, Ber. 1911, 44, 419).

2 : 5 : 6-**Tribromo-3 : 4-toluquinone**, m.p. 117°–118° (Cousin).

5-Hydroxy-3 : 4-toluquinone. Nitrosoorcinol $C_6H_2(CH_3)(NO)(OH)_2$ or

$C_6H_2(CH_3)(OH)(:NOH)O$

is the 4-oxime. *Dibenzoyl derivative*, m.p. 157°–158° (Henrich, Monatsh. 1897, 18, 169).

2 : 5-**Toluquinone.** By oxidation of 2 : 5-toluylenediamine (Nietzki, Ber. 1877, 10, 833) or *o*-toluidine (Ladenburg, *ibid.* 1128; Clark, Amer. Chem. J. 1892, 14, 565; Schniter, Ber. 1887, 20, 2283; Nietzki, Annalen, 1882, 215, 158); m.p. 68°–69°. Molecular heat of combustion at constant pressure, 805·3 cal. (Valeur, Compt. rend. 1897, 125, 872).

Resembles *p*-benzoquinone in most properties. On standing 24 hours with 2½ parts of sulphuric acid and 2½ parts of water, polymerises to 'isotoluquinone' $(C_7H_6O)_2$ (Spica, Gazz. chim. ital. 1882, 12, 225). Yields the triacetyl derivative of 2 : 4 : 5-trihydroxytoluene when heated with acetic anhydride and sulphuric acid (Thiele and Winter, Annalen, 1900, 311, 349).

Dichloride $C_7H_6Cl_2O_2$, m.p. 135°–136° (Clark); *dibromide*, m.p. 61°–62° (Clark).

Chloroimine $C_6H_3(CH_3)(:NCl)O$, m.p. 87°–88° from 5-amino-*o*-cresol (Hirsch, Ber. 1885, 18, 1514). *Chloroimine* from 6-amino-*m*-cresol, m.p. 75° (Städel and Kolb, Annalen, 1890, 259, 218).

Dimethylaminophenylimine

$O:C_6H_3(CH_3):N\cdot C_6H_4\cdot N(CH_3)_2$

(i.) From *o*-cresol and dimethyl-*p*-phenylenediamine, m.p. 123°; (ii.) from *m*-cresol, m.p. 117°–118° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1133; Dufet, Zeitsch. Kryst. 1897, 27, 631).

2 : 5-**Toluquinone-di-*p*-tolyldiimine**

$CH_3\cdot C_6H_3(:N\cdot C_6H_4\cdot CH_3)_2$.

By acting on an alcoholic solution of di-*p*-tolyl-2 : 5-toluylenediamine with concentrated ammoniacal copper nitrate. Orange-red needles, m.p. 145°–146°; dissolves with bright blue colour in concentrated sulphuric acid (Green, Ber. 1893, 26, 2781).

2 : 5-**Toluquinone-2-monoxime**

$C_6H_3(CH_3)(:NOH)O$

identical with nitroso-*m*-cresol.

Benzoyl derivative $C_{14}H_{11}O_3N_2$, m.p. 177°; gives a *dichloride* $C_{14}H_{11}O_3N_2Cl_2$, m.p. 149°, and *dibromide* $C_{14}H_{11}O_3N_2Br_2$, m.p. 159° (Bridge and Morgan, Amer. Chem. J. 1898, 20, 775; 1899, 22, 406).

2 : 5-**Toluquinone-5-monoxime,** identical with nitroso-*o*-cresol, m.p. 134°–135°. By adding the theoretical amount of nitrosyl sulphate to 1 part of *o*-cresol in 30 or 40 parts of water (Nölting and Kohn, Ber. 1884, 17, 370). From toluquinone and hydroxylamine (Goldschmidt and Schmied, *ibid.* 2063). Long needles, oxidised by ferricyanide to nitrocresol.

2 : 5-**Toluquinone dioxime** $C_6H_3(CH_3)(:NOH)_2$. By the action of hydroxylamine hydrochloride on either monoxime (Nietzki and Guitermann, Ber. 1888, 21, 432) or on 2 : 5-dinitroso-toluene (Mehne, *ibid.* 733). From 5-nitroso-2-ethyltoluidine (O. Fischer, Annalen, 1895, 286, 163). Explodes on heating.

Diacetyl derivative, m.p. 120°; *benzoyl derivative*, m.p. 135°–136°; and dibromide, m.p. 165° (Bridge and Morgan).

Monochlorotoluquinones and derivatives (Claus and Schweitzer, Ber. 1886, 19, 928; Claus and Jackson, J. pr. Chem. 1888, ii. 38, 328; Schniter, Ber. 1887, 20, 2286; Vorländer and Schrödter, *ibid.* 1901, 34, 1653; Kehrmann and Tichvinsky, Annalen, 1898, 303, 16; Oliveri-Tortorici, Gazz. chim. ital. 1897, 27, ii. 575; Morgan, Amer. Chem. J. 1899, 22, 407).

Dichlorotoluquinones $C_6H(CH_3)\cdot Cl_2O_2$ (Southwarth, Annalen, 1873, 168, 274).

Trichloro-2 : 5-toluquinone $C_6(CH_3)Cl_3O_2$, by chlorination of *o*- and *m*-cresol, m.p. 232° (Borgmann, Annalen, 1869, 152, 248; Southwarth, *ibid.* 1873, 168, 273; Claus and Hirsch, J. pr. Chem. 1889, ii. 39, 59; Claus and Riemann, Ber. 1883, 16, 1602; Hayduck, Annalen, 1874, 172, 209; Knapp and Schultz, *ibid.* 1881, 210, 176; Seelig, *ibid.* 1887, 237, 145; Elbs and Brunschweiler, J. pr. Chem. 1895, ii. 52, 559).

Tetrachloroquinone $C_6(CH_2Cl)Cl_3O_2$, m.p. 266°–270° (Gorup, Annalen, 1867, 143, 159; Braeuninger, *ibid.* 1877, 185, 352; Richter, Ber. 1901, 34, 4296).

Bromo-2:5-toluquinone $C_6H_2(CH_3)BrO_2$, 3-derivative, m.p. 93°; 4-derivative, m.p. 106° (Claus and Jackson, J. pr. Chem. 1888, ii. 38, 326; Schniter, Ber. 1887, 20, 2286; Gattermann, *ibid.* 1894, 27, 1931; Kehrmann and Rust, Annalen, 1898, 303, 25; Bridge, Amer. Chem. J. 1898, 20, 773; Morgan, *ibid.* 1899, 22, 405). *5-sulphono-derivative* of *3-bromotoluquinone* $C_6H_2(CH_3)Br(:SO_2)O$: a yellow solution is obtained by adding potassium acetate to an acetone solution of bromocresol-sulphonyl chloride. The sulphono-quinone is obtained in a colourless polymeric form (Zincke and Brune, Ber. 1911, 44, 188).

Dibromo-2 : 5-toluquinones $C_6H(CH_3)Br_2O_2$ (Canzoneri and Spica, Gazz. chim. ital. 1882, 12, 473; Claus and Dreher, J. pr. Chem. 1889, ii. 39, 370).

Tribromo-2 : 5-toluquinone $C_6(CH_3)Br_3O_2$, m.p. 235°–236° (Canzoneri and Spica, Gazz. chim. ital. 1882, 12, 470; Auwers and Ziegler, Hampe, v. Erggelet and Burrows, Ber. 1896, 29, 2350; 1899, 32, 3015, 3033, 3040).

Tetrabromo-2 : 5-toluquinone

$C_6(CH_2Br)Br_3O_2$,

m.p. 258°–259° (Auwers and Hampe, Ber. 1899, 32, 3015).

Pentabromo-2 : 5-toluquinone

$C_6(CHBr_2)Br_3O_2$,

m.p. 160° (Auwers and Burrows, Ber. 1899, 32, 3038).

Iodo- and **di-iodo-2 : 5-toluquinones** (Kehrmann, J. pr. Chem. 1889, ii. 39, 398, 401).

Chlorobromo-2 : 5-toluquinones
$C_6H(CH_3)ClBrO_2$
(Schniter, Ber. 1887, 20, 2287).

Nitro-2 : 5-toluquinone $C_6H_2(CH_3)(NO_2)O_2$, m.p. 237° (? *p*-nitrobenzoic acid, Étard, Ann. Chim. Phys. 1881, v. 22, 275). *Halogen derivatives* (Zincke, J. pr. Chem. 1901, ii. 63, 186).

3-Amino-2 : 5-toluquinone
$C_6H_2(CH_3)(NH_2)O_2$.
The hydrochloride of the 5-imine is obtained from diaminocresol dihydrochloride at −15°; it is light red in colour. At ordinary temperature the dark red hydrochloride of the 3-imine of 5-amino-2 : 3-toluquinone is obtained (Piccard, Ber. 1909, 42, 4332).

4-Amino-2 : 5-toluquinone
$C_6H_2(CH_3)(NH_2)O_2$.
Several derivatives are known.

Imine $C_6H_2(CH_3)(NH_2)(:NH)O$. Salts are obtained by oxidation of diamino-cresol
$(CH_3 : OH : NH_2 : NH_2 = 1 : 5 : 2 : 4)$
(Kehrmann and Prager, Ber. 1906, 39, 3440).

2-p-Tolylimine. From the di-*p*-tolylimine by the action of hydrogen chloride on its alcoholic solution at 25°, pouring into water and precipitating with sodium acetate. Small reddish-brown crystals, m.p. 143°–145° (Green, Ber. 1893, 26, 2775; compare Klinger and Pitschke, *ibid.* 1884, 17, 2442, and Barsilowsky, J. Russ. Phys. Chem. Soc. 1887, 19, 146).

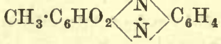
2-Phenyl-5-p-tolyldiimine, m.p. 204° (Green).

Di-p-tolyldiimine
$C_6H_2(CH_3)(NH_2)(:N\cdot C_7H_7)_2$.
360 grms. of potassium dichromate, 212 grms. of *p*-toluidine and 400 grms. of concentrated sulphuric acid in 40 litres solution in water are allowed to stand 2–3 hours at 5°. The raw product is dissolved in cold glacial acetic acid, diluted with water and saturated with sodium carbonate. The precipitate is then extracted with hot alcohol and crystallised from xylene. This compound has also been obtained by oxidation of *p*-tolidine and of *o*-amino-*m*, *p*-ditolylamine (Barsilowsky, Annalen, 1881, 207, 102; J. Russ. Phys. Chem. Soc. 1887, 19, 141; Perkin, Chem. Soc. Trans. 1880, 37, 546; Klinger and Pitschke, Ber. 1884, 17, 2440; Green, *ibid.* 1893, 26, 2774; Börnstein, *ibid.* 1901, 34, 1274). Dark red plates, m.p. 235°. Soluble in concentrated sulphuric acid with greenish-blue colour. On warming the solution, *p*-toluidine is split off, the colour changing to Bordeaux red. For other reactions, *see* references given.

Anilino-2 : 5-toluquinone
$C_6H_2(CH_3)(NHC_6H_5)O_2$.
Two isomers of m.p. 144°–145° (Hagen and Zincke, Ber. 1883, 16, 1559) and m.p. 148° ($\cdot NHC_6H_5$ in position 4 or 6), Jacobson, Annalen, 1895, 287, 151) are known.

Anilino-2 : 5-toluquinonephenylimine
$C_6H_2(CH_3)(NHC_6H_5)(:NC_6H_5)O$,
m.p. 151° (O. Fischer and Hepp, Annalen, 1890, 256, 259).

***o*-Nitroanilino-2 : 5-toluquinone**
$C_6H_2(CH_3)(NHC_6H_4NO_2)O_2$,
decomposes at 200° (Leicester, Ber. 1890, 23, 2796). Yields quinonephenotolazine


$$CH_3\cdot C_6HO_2\left\langle \begin{matrix} N \\ \dot{N} \end{matrix} \right\rangle C_6H_4$$

with alcoholic ammonium sulphide at 100°.

Toluidino-2 : 5-toluquinones
$C_6H_2(CH_3)(NHC_7H_7)O_2$
and derivatives (Jacobson, Annalen, 1895, 287, 192, 198; Leicester, Ber. 1890, 23, 2796; Börnstein, *ibid.* 1901, 34, 1274, 4348; compare Perkin, Ber. 1880, 13, 1874).

Diethyl diglycino-2 : 5-toluquinone, m.p. 162°. From ethyl glycine and toluquinone in alcoholic solution (E. Fischer and Schrader, Ber. 1910, 43, 525).

Dianilino-*p*-toluquinone
$C_6H(CH_3)(NHC_6H_5)_2O_2$.
From aniline and toluquinone in alcoholic solution, m.p. 232°–233° (Hagen and Zincke, Ber. 1883, 16, 1559). *Phenylimine*, m.p. 167° (Hagen and Zincke) or 172°–173° (O. Fischer and Hepp, Ber. 1888, 21, 678).

Ditoluidinotoluquinones
$C_6H(CH_3)(NHC_7H_7)_2O_2$
and derivatives (O. Fischer and Hepp, *ibid.* 1888, 21, 679; Annalen, 1890, 256, 259; 1891, 262, 251).

3-Hydroxy-2 : 5-toluquinone
$C_6H_2(CH_3)(OH)O_2$.
The 2-*oxime* is identical with nitrosoorcinol. Red prisms giving a yellow modification on heating, transition point 128°. Possibly the two modifications are ketonic and enolic forms (Henrich, Monatsh. 1897, 18, 142; Ber. 1897, 29, 989; Zeitsch. physikal. Chem. 1897, 24, 187; Farmer and Hantzsch, Ber. 1899, 32, 3108; Hantzsch and Sluiter, *ibid.* 1906, 39, 162).

4-Hydroxy-2 : 5-toluquinone, m.p. 142°. By oxidation of 2 : 4 : 5-trihydroxytoluene with ferric chloride. *Acetyl- derivative,* m.p. 75°–76° (Thiele and Winter, Annalen, 1900, 311, 350). *Halogen- derivatives* (Spica and Magnanini, Gazz. chim. ital. 1883, 13, 312; Henrich, Taubert and Birkner, Ber. 1912, 45, 303).

Anilinohydroxy-2 : 5-toluquinone decomposes at 250°, its *phenylimine; methyl ether,* m.p. 131°; *ethyl ether,* m.p. 115°–116°; and *isobutyl ether,* m.p. 117°, have been prepared (Hagen and Zincke, Ber. 1883, 16, 1560).

Ethoxy-2 : 5-toluquinone is known as the p-*tolylimine,* m.p. 76° (Jacobson and Piepenbrink, Ber. 1894, 27, 2710).

3 : 6-Dihydroxy-2 : 5-toluquinone
$C_6H(CH_3)(OH)_2O_2$,
m.p. 177°. From anilinohydroxytoluquinonephenylimine and dilute aqueous potash (Hagen and Zincke, Ber. 1883, 16, 1562).

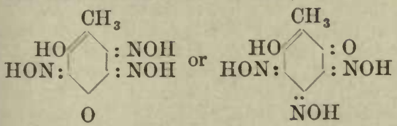
Chlorodihydroxy-2 : 5-toluquinone (Knapp and Schultz, Annalen, 1881, 210, 177; Levy and Bickel, *ibid.* 1889, 249, 69).

Dichlorodihydroxytoluquinone (Braeuninger, Annalen, 1877, 185, 354).

4-Nitro-3 : 6-dihydroxy-2 : 5-toluquinone (*tolunitranilic acid*), $C_6(CH_3)(NO_2)(OH)_2O_2$. From the potassium salt which is obtained by the action of potassium nitrite on trichlorotoluquinone. Melts and decomposes at 180° (Kehrmann and Brasch, J. pr. Chem. 1889, ii. 39, 378).

Trihydroxy-2 : 5-toluquinone
$C_6(CH_3)(OH)_3O_2$.
By action of hydrochloric acid on aminodiiminoorcinol hydrochloride. *Triacetyl derivative* (Merz and Zetter, Ber. 1879, 12, 2044).

Toluene-diquinone $C_6H(CH_3)O_4$. Known as *tri-* and *tetra-oximes*. The former,



m.p. 189°–190°, is obtained by the action of hydroxylamine hydrochloride on dinitrosomethylphloroglucinol (Weidel and Pollak, Monatsh. 1900, 21, 58).

Ethyl-*p*-benzoquinone $C_6H_3(C_2H_5)O_2$, from ethyl indophenol; m.p. 38·2° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1130).

2-Ethyl-3 : 5 : 6-tribromo-*p*-benzoquinone, m.p. 118°–120° (Zincke, Ber. 1901, 34, 255).

1 : **2-Dimethyl-4 : 5-benzoquinone** $C_6H_2(CH_3)_2O_2$. By oxidising 5-amino-4-hydroxy-1 : 2-xylene in dilute sulphuric acid with potassium dichromate. Red crystals, m.p. 102°; far more stable than *o*-benzoquinone (Diepolder, Ber. 1909, 42, 2921). *Dichlorodiimine* $C_6H_2(CH_3)_2(:NCl)_2$, explodes at 87° (Noelting and Thesmar, Ber. 1902, 35, 643).

1 : 3-Dimethyl-4 : 5-benzoquinone. The *dioxime* $C_6H_2(CH_3)_2(:NOH)_2$, m.p. 142°, is obtained by reducing dinitrosoxylene with hydroxylamine (Zincke and Schwarz, Annalen, 1899, 307, 48): anhydride, *xylylenefurazane*, m.p. 60°.

2 : 6-**Dichloro-1 : 3-dimethyl-4 : 5-benzoquinone,** m.p. 108° (Francke, Annalen, 1897, 296, 206).

1 : 2-**Dimethyl-3 : 6-benzoquinone** (*o-xyloquinone*), m.p. 55° (Noelting and Forel, Ber. 1885, 18, 2673); *dichlorodiimine*, m.p. 105·5° (Noelting and Thesmar, *ibid.* 1902, 35, 649).

4 : 5-**Dichloro-1 : 3-dimethyl-4 : 5-benzoquinone,** m.p. 159° (Claus and Berkefeld, J. pr. Chem. 1891, ii. 43, 584).

1 : **3-Dimethyl-4 : 5-benzoquinone,** m.p. 72°–73° (Noelting and Baumann and Forel, Ber. 1885, 18, 1151, 2679). *Dichlorodiimine*, m.p. 112° (Noelting and Thesmar); *halogen-, hydroxy-derivatives*, &c. (Fittig and Siepermann, Annalen, 1876, 180, 27; Jacobsen, *ibid.* 1879, 195, 271; Claus and Runschke, J. pr. Chem. 1890, ii. 42, 124; Klages, Ber. 1896, 29, 314; Brunnmayd, Monatsh. 1900, 21, 9; Bose, *ibid.* 1027).

1 : 4-**Dimethyl-2 : 5-benzoquinone** (p-*xyloquinone* or *phlorone*), $C_6H_2(CH_3)_2O_2$, has been obtained from the higher homologues of phenol contained in coal-tar (Rommier and Bouilhon, Jahresb. 1862, 322; Carstanjen, J. pr. Chem. 1881, ii. 23, 423) and beech-tar (Rad, Annalen, 1869, 151, 158) by distillation with manganese dioxide and dilute sulphuric acid. Also by oxidising diamino-*p*-xylene (Nietzki, *ibid.* 1882, 215, 168); *p*-xylidine (Carstanjen; Noelting, Witt and Forel, Ber. 1885, 18, 2667); and pseudocumidine (Noelting and Baumann, *ibid.* 1885, 18, 1151). Synthesised by warming butane-dione (diacetyl) with excess of dilute caustic soda solution (v. Pechmann, *ibid.* 1888, 21, 1420), m.p. 125°; triclinic (Muthmann, Jahresb. 1889, 1634). *Dichlorodiimine*, m.p. 137° (Noelting and Thesmar, Ber. 1902, 35, 649). *Indophenol*

$$O:C_6H_2(CH_3)_2:N{\cdot}C_6H_4{\cdot}N(CH_3)_2,$$

m.p. 125°–126° (Bayrac, Bull. Soc. chim. 1894, iii. 11, 1134; Dufet, Ann. Chim. Phys. 1897, vii. 10, 58). *Monooxime* $C_6H_2(CH_3)_2(:NOH)O$, identical with nitroso-*p*-xylenol, long red needles, m.p. 165° (Oliveri, Gazz. chim. ital. 1882, 12, 162; H. Goldschmidt and Schmid, Ber. 1885, 18, 568; Salkowski, *ibid.* 1887, 20, 978; Pflug, Annalen, 1889, 255, 174). *Dioxime*, m.p. 254° (Sutkowski, Ber. 1887, 20, 978; Pflug); *diacetyl-derivative*, m.p. 170°.

Halogen derivatives of phlorone; *see* Carstanjen, Rad, Auwers and Baum (Ber. 1896, 29, 2341); Auwers and Sheldon (Annalen, 1898, 301, 276); Auwers and Rapp (*ibid.* 1898, 302, 165); Auwers and Sigel (Ber. 1902, 35, 436); Teichner (*ibid.* 2303).

Dihydroxy-*p*-xyloquinone $C_6(CH_3)_2(OH)_2O_2$. By condensation of ethyl oxalate and propionate with sodium; m.p. 245°. *Di-acetyl derivative*, m.p. 146·5° (Fichter and Willmann, Ber. 1904, 37, 2384; Annalen, 1908, 361, 363).

Dianilino-*p*-xyloquinone, m.p. 264° (Pflug, Annalen, 1889, 255, 171).

1 : 2 : 4-Trimethyl-5 : 6-benzoquinone. The *monochloro- derivative* $C_6Cl(CH_3)_3O_2$ obtained from trimethylchlorocatechol, m.p. 96°–97° (Hodes, Annalen, 1897, 296, 218).

1-**Propyl-2 : 5-benzoquinone.** *Methoxy-derivative* $C_6H_2(OCH_3)(C_3H_7)O_2$, m.p. 111°, by reducing an alcoholic solution of asarone with sodium (Ciamician and Silber, Ber. 1890, 23, 2294).

1-**Isopropyl-2 : 5-benzoquinone**

$$C_6H_3[CH(CH_3)_2]O_2,$$

m.p. 28·4° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 984). Derivatives (Hoffmann, Ber. 1901, 34, 1559; Böters, *ibid.* 1902, 35, 1505).

1-Methyl-4-ethyl-2 : 5-benzoquinone

$$C_6H_2(CH_3)(C_2H_5)O_2,$$

m.p. 55·3°, and *dimethylaminophenylimine*, m.p. 77° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 897).

1 : 2 : **4-Trimethyl-3 : 6-benzoquinone** (*cumoquinone*), m.p. 11° (Noelting and Baumann, Ber. 1888, 18, 1152; Nietzki and Schneider, Ber. 1894, 27, 1430). *Oxime*, m.p. 184°; *5-chloro-derivative*, m.p. 72°–73°; *5-nitro-derivative*, m.p. 113° (Nef, Annalen, 1887, 237, 17).

1-Methyl-4-propyl-2 : 5-benzoquinone

$$C_6H_2(CH_3)(C_3H_7)O_2,$$

m.p. 18° (Bayrac, Bull. Soc. chim. 1895, iii. 13, 979). *Dibromo- derivative*, m.p. 30° (Claus and Herfeldt, J. pr. Chem. 1891, ii. 43, 579).

1-Methyl-2-isopropyl-3 : 6-benzoquinone

$$C_6H_2[CH_3][CH(CH_3)_2]O_2,$$

m.p. 40° (Claus and Raps, J. pr. Chem. 1891, ii. 43, 576).

1-Methyl-3-isopropyl-2 : 5-benzoquinone, m.p. 32° (Claus and Herfeldt, *l.c.*).

Thymoquinone $C_6H_2(CH_3)(i\text{-}C_3H_7)O_2$, m.p. 45·5°, has been found in the oil of wild bergamot, *Monardia fistulosa* (Brandel and Kremers, Pharm. Review, 1901, 19, 200, 244). Obtained from thymol (Lallemand, Jahresb. 1854, 592); cymophenol $C_6H_3(CH_3)(C_3H_7)(OH)$ (Carstanjen, J. pr. Chem. 1877, ii. 15, 410) and dithymolethane $CH_3{\cdot}CH(C_{10}H_{12}OH)_2$ (Steiner, Ber. 1878, 11, 289) by distillation with manganese dioxide and dilute sulphuric acid, or by the oxidation of aminothymol (Andresen, J. pr. Chem. 1881, ii. 23, 172; Armstrong, Ber. 1877, 10, 297; Liebermann and Ilinski, *ibid.* 1885, 18, 3194).

By the hydrolysis of the indophenol from dimethyl-*p*-phenylenediamine and thymol (Bayrac, Bull. Soc. chim. 1892, iii. 7, 99); by oxidation of carvacrol with chromic acid mixture (Reychler, Bull. Soc. chim. 1892, iii. 7, 32); and by oxidation of thymohydroquinone with benzoquinone (Biltris, Bull. Acad. roy. Belge, 1898, iii. 35, 44; Valeur, Ann. Chim. Phys. 1900, vii. 21, 553); m.p. 45·5°; b.p. 232°; heat of combustion 1274.6 cal. (Valeur, Compt. rend. 1897, 125, 872). For other properties and reactions, *see* Liebermann (Ber. 1885, 18, 3196), Ciamician and Silber (Real. Accad. d. Linc. 1901, v. 10, i. 96), Jackson and Oenslager (Amer. Chem. J. 1896, 18, 20), Biltris (*l.c.*), Valeur (*l.c.*).

Thymoquinone gives *bithymoquinone*, a polymer of m.p. 200°–201°, when its ethereal solution is exposed to light; it is largely reconverted into thymoquinone on distillation (Liebermann and Ilinski, Ber. 1885, 18, 3195), and gives an oxime, m.p. 264° and dioxime, m.p. 290°, differing from those of thymoquinone.

Two *thymoquinonedimethylaminophenylimines* $O:C_6H_2(CH_3)(C_3H_7):N{\cdot}C_6H_4{\cdot}N(CH_3)_2$ are known, (i.) from thymol and dimethyl-*p*-phenylenediamine (N=5), melts at 69·5°; (ii.) from carvacrol (N=2) at 87°–88° (Bayrac, Bull. Soc. chim. 1892, iii. 7, 97; 1894, iii. 11, 1135; Dufet, Zeitsch. Kryst. 1897, 27, 631).

Thymoquinone-chloroimine

$$C_6H_2(CH_3)(C_3H_7)(O)(HCl)$$

explodes at 160°–170° (Andresen, J. pr. Chem. 1881, ii. 23, 169).

Thymoquinone-2-oxime

$$C_6H_2(CH_3)(C_3H_7)(O)(:NOH)$$

identical with nitrosothymol, m.p. 160°–162° (R. Schiff, Ber. 1875, 8, 1500; Goldschmidt and Schmied, *ibid.* 1884, 17, 2061; Liebermann and Ilinski, *ibid.* 1885, 18, 3194; Widmann, *ibid.* 1882, 15, 171; Liebermann, *ibid.* 1877, 10, 78; Sutkowski, *ibid.* 1886, 19, 2315; Plancher, Gazz. chim. ital. 1895, 25, ii. 385; Oliveri-Tortorici, *ibid.* 1897, 27, ii. 580; Valeur, Bull. Soc. chim. 1898, iii. 19, 516; Klages, Ber. 1899, 32, 1518).

Thymoquinone-5-oxime, identical with nitroso-carvacrol, m.p. 153° (Mazzara and Plancher, Gazz. chim. ital. 1891, 21, ii. 155; Paternò and Canzoneri, Ber. 1879, 12, 383; Plancher, Gazz. chim. ital. 1895, 25, ii. 391; Klages, Ber. 1899, 32, 1518). 3-*Chloro-derivative*, m.p. 157°–158° (Oliveri-Tortorici, Gazz. chim. ital. 1897, 27, ii. 582; Kehrmann, Krüger and Schön, Annalen, 1900, 310, 95, 108; Stroesco, Zeitsch. Kryst. 1899, 30, 75).

Thymoquinone-dioxime

$$C_6H_2(CH_3)(C_3H_7)(:NOH)_2$$

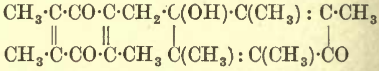
has been obtained from nitrosothymol (Kehrmann and Messinger, Ber. 1890, 23, 3558) or nitrosocarvacrol and hydroxylamine (Oliveri-Tortorici, Gazz. chim. ital. 1900, 30, i. 534). Does not melt; decomposes at 255° (Kehrmann and Messinger) or at 235° (Oliveri-Tortorici). *Acetyl-derivative* (Böhm, Ber. 1895, 28, 1547); and *diacetyl-derivative*, two modifications, each melting at 110°.

Numerous *halogen, alkylamino-*, anilino-, &c., derivatives of thymoquinone have been prepared; for literature, *see* Andresen (J. pr. Chem. 1881, ii. 23, 178); Schniter (Ber. 1887, 20, 1317); Carstanjen (J. pr. Chem. 1871, ii. 3, 55); Mazzara and Discalzo (Gazz. chim. ital. 1886, 16, 197); Kehrmann (Ber. 1889, 22, 3264; J. pr. Chem. 1889, ii. 39, 394; 1889, ii. 40, 188); Zincke (Ber. 1881, 14, 94); H. Schulz (*ibid.* 1883, 16, 900); Anschütz and Leather (Annalen, 1887, 237, 115); Ladenburg (Ber. 1877, 10, 49, 1220); Liebermann (*ibid.* 1877, 10, 79, 613); Mazzara (*ibid.* 1890, 23, 1392); Kowalski (*ibid.* 1892, 25, 1661); Kehrmann and Krüger (Annalen, 1900, 310, 89); Stroesco (Zeitsch. Kryst. 1899, 30, 75); Hoffmann (Ber. 1901, 34, 1558); Böters (*ibid.* 1902, 35, 1505).

Dihydroxythymoquinone, m.p. 220°–221°. *Diacetate*, m.p. 81°; *Dibenzoate*, m.p. 163°.

1 : 4-**Diethyl** - 3 : 6 - **dihydroxy** - 2 : 5 - **benzoquinone**, m.p. 217°–218°. *Diacetate*, m.p. 130°; *dibenzoate*, m.p. 201° (Fichter, Annalen, 1908, 361, 363).

Tetramethyl-*p*-benzoquinone or **duroquinone** $C_6(CH_3)_4O_2$ is obtained by the oxidation of diaminodurene with ferric chloride (Nef, Annalen, 1887, 237, 5). For a convenient method of preparation, starting with pseudo-cumene and converting this by the Friedel-Crafts reaction into durene, *see* Rügheimer and Hankel (Ber. 1896, 29, 2172). Also obtained from pentane-2 : 3-dione (von Pechmann, *ibid.* 1888, 21, 1420) and 3, 3-dichloropentane-2-one (Fawørsky, J. pr. Chem. 1895, ii. 51, 538), m.p. 111°. Yields *biduroquinone*,



$$\begin{array}{l}CH_3{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH_2{\cdot}C(OH){\cdot}C(CH_3):C{\cdot}CH_3\\ \qquad\ \ \| \qquad\ \ \| \qquad\quad\ | \qquad\qquad\qquad\quad\ |\\ CH_3{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH_3\ C(CH_3):C(CH_3){\cdot}CO\end{array}$$

m.p. 202°–203°, on standing with alcoholic potash (Rügheimer and Hankel, *l.c.*); various derivatives of the polymer have been prepared.

1 : 4-**Di-isopropyl**-3 : 6-**dihydroxy**-2 : 5-**benzoquinone**, m.p. 184°. *Diacetate*, m.p. 137·5°; *dibenzoate*, m.p. 220°.

1 : 4 - **Di**-*n*-**butyl**-3 : 6-**dihydroxy**-2 : 5-**benzoquinone**, m.p. 175°; *diacetate*, m.p. 60° (Fichter).

Di-tertiary-butyl-*p*-benzoquinone

$$C_6H_2[C(CH_3)_3]_2O_2$$

from quinol and tertiary butyl chloride in presence of ferric chloride, m.p. 150°–151° (Garewitsch, Ber. 1899, 32, 2427).

1 : 4-**Di-isobutyl** - 3 : 6 - **dihydroxy**-2 : 5-**benzoquinone**, m.p. 217°–218°. By condensation of ethyl isocaproate and ethyl oxalate by sodium (Fichter, Jetzer and Leepin, Annalen, 1913, 395, 2). *Diacetyl- derivative*, m.p. 113·5°.

Di-isoamyl-*p*-benzoquinone

$$C_6H_2[CH_2{\cdot}CH_2{\cdot}CH(CH_3)_2]_2O_2$$

from diisoamylquinol, m.p. 140° (Königs and Mai, Ber. 1892, 25, 2653).

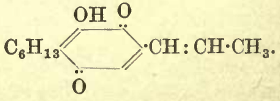
1 : 4-**Di**-*n*-**pentyl** - 3 : 6 - **dihydroxy**-2 : 5-**benzoquinone**, m.p. 164°. *Diacetyl- derivative*, m.p. 74°.

1 : 4 - **Di**-*n*-**hexyl** - 3 : 6 - **dihydroxy**- 2 : 5-**benzoquinone**, m.p. 154°. *Diacetyl- derivative*, m.p. 68°.

1 : 4 - **Di**-*n*-**heptyl** - 3 : 6 - **dihydroxy**-2 : 5 - **benzoquinone**, m.p. 145°. *Diacetyl- derivative*, m.p. 77·5°.

1 : 4-**Di** - *n* - **octyl** - 3 : 6 - **dihydroxy**-2 : 5-**benzo**quinone, m.p. 141° (Fichter, Jetzer and Leepin, *loc. cit.*).

Perezone (*Pipitzahoic acid*),



Discovered by Rio de la Loza in the Mexican drug *Raíz del Pipitzahuac* or *Radix Pereziae;* m.p. 104°. Yields *anilino-* and *hydroxy- derivatives* (Weld, Annalen, 1855, 95, 188; Anschütz, Ber. 1885, 18, 709; Annalen, 1887, 237, 90; Fichter, Jetzer and Leepin, *ibid.* 1913, 395, 15).

Phenyl-*p*-benzoquinone $C_6H_3(C_6H_5)O_2$ is obtained by oxidation of 5-amino-2-hydroxydiphenyl with chromic acid mixture (Borsche, Ber. 1899, 32, 2937; Annalen, 1900, 312, 220; Hill and Hale, Ber. 1900, 33, 1242); m.p. 112°–113°. Several derivatives are known; *see* also Jackson and Koch (Amer. Chem. J. 1901, 26, 23). Phenylbenzoquinone is isomeric with diphenoquinone $O:C_6H_4:C_6H_4:O$ (*vide infra*).

1 : 3-Diphenyl-2 : 5-benzoquinone

$$C_6H_2(C_6H_5)_2O_2,$$

m.p. 137°–138° (Borsche, Ber. 1899, 32, 2938: Annalen, 1900, 312. 230); m.p. 135°–136° (corr.) (Hill, Amer. Chem. J. 1900, 24, 8; Hill and Soch, Ber. 1900, 33, 1241). The *monoxime* and its benzoyl derivative have been prepared, whilst 4-*anilino*-1 : 3-diphenylbenzo-2 : 5-quinone m.p. 167°, is formed when the quinone is boiled with aniline.

1 : 4-Diphenyl-2 : 5-benzoquinone

$$C_6H_2(C_6H_5)_2O_2,$$

m.p. 214°. By alkaline condensation of methylphenyldiketone. Orange yellow leaflets (Müller and von Pechmann, Ber. 1889, 22, 2131). Diphenyldihydroxy-*p*-benzoquinone and Dibenzyldihydroxy-*p*-benzoquinone (Fichter, Annalen, 1908, 361, 363).

1 : 4-Dibenzhydryl-2 : 5-benzoquinone

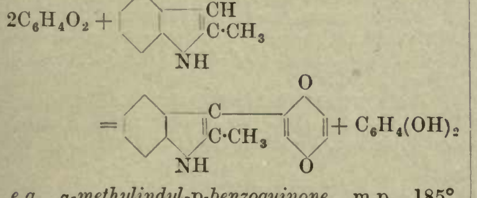
$$C_6H_2[CH(C_6H_5)_2]_2O_2.$$

By condensation of benzoquinone with benzhydrol, m.p. 250° (indef.) (Möhlau, Ber. 1898, 31, 2351; Möhlau and Klopfer, *ibid.* 1899, 32, 2147). The *octamethyltetraamino- derivative*

$$C_6H_2[CH\{C_6H_4{\cdot}N(CH_3)_2\}_2]_2$$

is obtained by warming benzoquinone with Michler's hydrol for 6 hours in alcoholic solution; m.p. 245°.

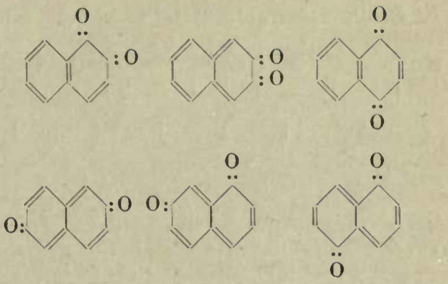
Other substituted benzoquinones are obtained by the action of substances of the indole series on quinone. Thus α-methylindole reacts as follows:



e.g. *α-methylindyl*-p-*benzoquinone*, m.p. 185°. N-*methyl-α-methylindyl*-p-*benzoquinone*, m.p. 160°; *α-phenylindyl*-p-*benzoquinone*, m.p. 205°, and other substances. Tetrahydroquinoline also reacts, giving $C_6H_2(C_9H_{10}N)_2O_2$, m.p. 189° (Möhlau and Redlich, Ber. 1911, 44, 3605).

QUINONES $C_nH_{2n-14}O_2$.

Naphthaquinones. Six naphthaquinones are possible



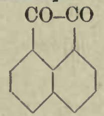
The 1 : 2-, 1 : 4-, and 2 : 6-quinones have been prepared. The first two have been known for a long period, the 2 : 6-quinone was obtained by Willstätter and Parnas (Ber. 1907, 40, 1406, 3971). See article on NAPHTHALENE.

QUINONES $C_nH_{2n-16}O_2$.

Phenylquinone $C_6H_3(C_6H_5)O_2$ is dealt with earlier in this article.

QUINONES $C_nH_{2n-18}O_2$.

Acenaphthenequinone $C_{12}H_6O_2$, or



m.p. 262°–263°.

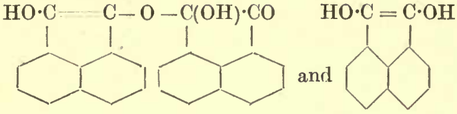
This compound is not strictly a quinone, the two carbonyl groups being situated in a 5-membered ring. It has been prepared by oxidation of acenaphthene $C_{12}H_{10}$ with chromic acid mixture, &c.; the yields are not, however, good (Graebe, Ber. 1887, 20, 659; Graebe and Gfeller, *ibid.* 1892, 25, 654; Annalen, 1893, 276, 1). Better results have been obtained by hydrolysing the monooxime obtained by the action of alkyl nitrites on acenaphthene.

When four molecular proportions of amyl nitrite are added to a boiling solution of acenaphthene whilst a stream of hydrogen chloride is passed in, two isomeric acenaphthenequinoneoximes $C_{12}H_6(:NOH)O$ are produced. These may be separated by difference of acidity, one being insoluble in hot sodium carbonate solution. When this is rapidly crystallised from glacial acetic acid, small pale yellow crystals which decompose at 207° are obtained. If the boiling with acetic acid be continued some time, water precipitates the oxime of m.p. 230°, which can be obtained from acenaphthenequinone and hydroxylamine (Francesconi and Pirazzoli, Gazz. chim. ital. 1903, 33, i. 42).

To prepare acenaphthene quinone, the oxime of higher m.p. is dissolved in 7 times its weight of 75 p.c. sulphuric acid and heated for 1 hour on the water-bath. Water is added, the quinone filtered off, digested for some time with warm dilute caustic soda and recrystallised from glacial acetic acid (Kalle and Co., D. R. P. 228698, 1909; Reissert, Ber. 1911, 44, 1749). For the oxime, m.p. 220° is given.

Acenaphthene quinone yields a compound $C_{12}H_6(C_6H_5)_2O$ (diphenylacenaphthenone) with benzene and aluminium chloride (Zsuffa, Ber. 1910, 43, 2915); on reduction compounds of m.p. 248° and 254° are produced (Kalle and Co.,

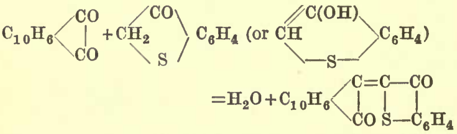
D. R. P. 224979, 1909) to which the constitutions



have been assigned.

Acenaphthenequinone condenses with substances containing a reactive methylene group. Vat dyestuffs may be produced in this way.

Ciba-scarlet G or *Thioindigo scarlet G* is obtained by condensation with 3-hydroxy (1) thionaphthene

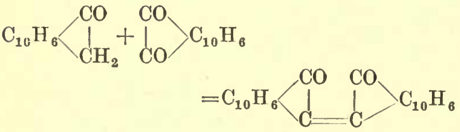


or by heating to 230°–250° with phenylthiolglycol-*o*-carboxylic acid (Basler Chemische Fabrik, D. R. P. 205377, 1907; compare Bezdzik and Friedländer, Monatsh. 1908, 29, 375; A. Grob, Ber. 1908, 41, 3331). The acenaphthene quinone may be replaced by dichloroacenaphthenone. The following patents refer to similar considerations (Basler Chemische Fabrik, D. R. PP. 196349, 1907; 198510, 1907; Ges. chem. Ind. Basel, D. R. PP. 210905, 1907; 211696, 1907; 212870, 1908; 213504, 1908).

Ciba scarlet is a yellowish-red powder, sublimes on heating, gives a green solution in concentrated sulphuric acid and is precipitated as red flocks by addition of water. It is used as a vat dyestuff (sodium hyposulphite or sodium sulphide) and in cotton printing.

Ciba red R paste (D. R. P. 213504) is a brominated ciba-scarlet G; its reactions are similar (Grandmougin, Elsässischer Textil-Blatt, 1911).

By the condensation of acenaphthenequinone with acenaphthenone, an orange-red dyestuff, probably identical with the 'biacenaphthylidenedione' of Graebe and Gfeller (Annalen, 1893, 276, 17) and Graebe and Jequier (*ibid.* 1896, 290, 199), is obtained



The condensation can be effected in absolute alcoholic solution with sodium carbonate or sodium acetate and acetic anhydride may be used (Ges. chem. Ind. Basel, D. R. P. 212858, 1908).

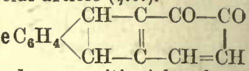
18 parts of acenaphthenequinone, 16·5 parts of acenaphthenone and 3 parts of fused sodium acetate are heated with 100 parts of acetic anhydride to boiling under reflux. The product separates as orange-needles which are collected after cooling, washed and dried.

Acenaphthenone itself may be conveniently prepared by treating α-naphthylacetyl chloride in nitrobenzene with aluminium chloride dissolved in the same solvent (Badische Anilin- und Soda-Fabrik, D. R. P. 230237, 1909).

QUINONES $C_nH_{2n-20}O_2$.

Anthraquinone $C_{14}H_8O_2$ and its derivatives are described in a special article (*q.v.*).

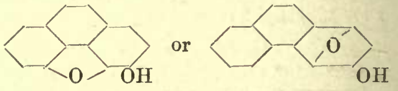
1 : 2-Anthraquinone



m.p. about 180° (with decomposition) has been obtained by the oxidation of 1-amino-2-hydroxyanthracene (Lagodzinski, Ber. 1894, 27, 1438; 1895, 28, 1422).

Phenanthraquinone and its derivatives are described in a special article (*v.* PHENANTHRENE).

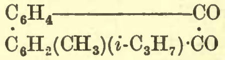
Morphenolquinone $C_{14}H_6O_4$, corresponds to morphenol $C_{14}H_7(OH)O$, which may be written constitutionally as



Vongerichten (Ber. 1900, 33, 352); Schryver and Lees (Chem. Soc. Trans. 1901, 79, 568).

Morphenol is obtained by the action of alcoholic potash on methylmorphimethine, acetylmorphenol when oxidised yields a quinone which furnishes morphenolquinone on hydrolysis. Orange aggregates from glacial acetic acid.

Retenequinone $C_{18}H_{16}N_2$ or



$$\begin{array}{l} C_6H_4\text{————————}CO \\ C_6H_2(CH_3)(i\text{-}C_3H_7)\cdot CO \end{array}$$

by oxidation of retene with chromic acid (Wahlforss, Zeitsch. Chem. 1869, 73), preferably in acetic acid solution (Bamberger and Hooker, Annalen, 1885, 229, 117). Orange needles, m.p. 197°–197·5°. Very easily soluble in boiling carbon disulphide; for solubility in alcohol *see* Ekstrand (*ibid.* 1877, 188, 75). Molecular heat of combustion at constant pressure, 2158·0 cal. (Valeur, Bull. Soc. chim. 1898, [iii.] 19, 514). *Perchlorate* $(C_{18}H_{16}O_2)_2\cdot HClO_4$ (Hofmann, Metzler and Lecher, Ber. 1910, 43, 182). Yields retene-ketone (1-methyl-4-methoethylfluorenone) on heating with barium hydroxide (Ekstrand, *ibid.* 1884, 17, 692). Shows the usual reactions of an *o*-quinone (azine formation, &c.); with arylhydrazine-sulphonic acids orange-red to blue-red dyestuffs are produced (A.-G. Chem. Ind. Rheinau; D. R. P. 46746, 1888). *Imine*, m.p. 109°–111° (Bamberger and Hooker); *oxime*, m.p. 128·5° (B. and H.).

Monobromoretene-quinone $C_{18}H_{15}O_2Br$, m.p. 210°–212° (Wahlforss). *Dibromoretene-quinone* $C_{18}H_{14}O_2Br_2$, m.p. 250°–252° (Bamberger and Hooker).

Diethylreteneindandione gives a quinone $C_{25}H_{24}O_4$, m.p. 193°–194°, on oxidation (Freund and Fleischer, Annalen, 1910, 373, 291).

QUINONES $Z_nH_{2n-22}O_2$.

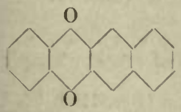
Fluoranthenequinone $C_{15}H_8O_2$, m.p. 188°, by oxidation of fluoranthene with chromic acid mixture: small red needles (Goldschmiedt, Ber. 1877, 10, 2029; Fittig, Gebhard, Liepmann, Annalen, 1878, 193, 149; 1880, 200, 3).

QUINONES $C_nH_{2n-24}O_2$.

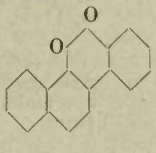
Diphenylbenzoquinone $C_6H_2(C_6H_5)_2O_2$. Has been described previously.

QUINONES $C_nH_{2n-26}O_2$.

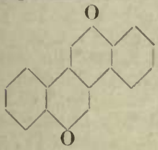
Many quinones $C_{18}H_{10}O_2$ are possible and the following have been obtained.



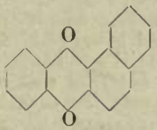
Naphthacenequinone.



1 : 2-Chrysoquinone.

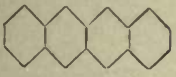


2 : 8-Chrysoquinone.

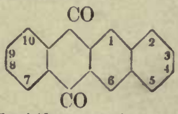


Naphthanthraquinone.

Naphthacenequinone $C_{18}H_{10}O_2$, is a para-quinone showing considerable analogy to anthraquinone: it is derived from a parent hydrocarbon naphthacene $C_{18}H_{12}$. The constitutional formulæ of these two compounds and the method of numbering the positions in the naphthacenequinone molecule are shown below.

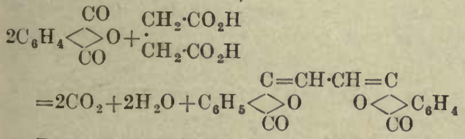


Naphthacene.



Naphthacenequinone.

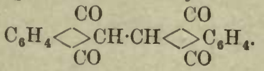
Gabriel and Michael melted a mixture of phthalic anhydride, succinic acid and fused sodium acetate and obtained ethylene (di)phthalide (Ber. 1877, 10, 1558)



$$2C_6H_4\begin{matrix}CO\\<>\\CO\end{matrix}O+\begin{matrix}CH_2\cdot CO_2H\\ \cdot\\ CH_2\cdot CO_2H\end{matrix}$$

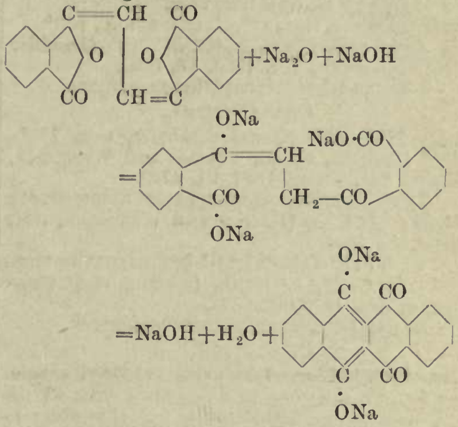
$$=2CO_2+2H_2O+\begin{array}{ccc} & C{=}CH\cdot CH{=}C & \\ C_6H_5<>O & & O<>C_6H_4\\ CO & & CO\end{array}$$

Roser examined the reaction and found that an *iso*-ethylene diphthalide was formed at the same time in small quantity (Ber. 1884, 17, 2774). Gabriel and Leupold improved the method for obtaining the ethylene phthalide (*ibid.* 1898, 31, 1161) and also examined the action of sodium methoxide on ethylene diphthalide which had been previously studied by F. Nathanson (*ibid.* 1893, 26, 2582). Nathanson suspended ethylene phthalide in methyl alcohol, added sodium methoxide, evaporated off the methyl alcohol, added hot water, separated from undissolved mattter and precipitated the filtrate with hydrochloric acid. The substance so obtained gave results on analysis agreeing with the expected *bis*-diketohydrindene,

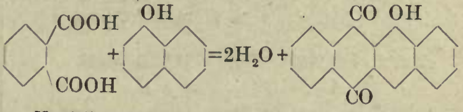


$$C_6H_4\begin{matrix}CO\\<>\\CO\end{matrix}CH\cdot CH\begin{matrix}CO\\<>\\CO\end{matrix}C_6H_4.$$

Gabriel and Leupold recognised that Roser's *iso*ethylene diphthalide was also formed in the reaction (Ber. 1898, 31, 1272) and found that it contained two hydroxyl groups. On distillation with zinc dust, hydrocarbons $C_{18}H_{12}$ and $C_{18}H_{14}$ were obtained. The latter evidently contains two CH_2-groups, since on oxidation with chromic acid, a quinone $C_{18}H_{10}O_2$ is produced. This quinone when fused with potash gives benzoic and β-naphthoic acids (anthraquinone when fused with potash gives two molecules of benzoic acid (Graebe and Liebermann, Annalen, 1871, 160, 129), which points to the formula given above for naphthacenequinone. The '*iso*ethylenediphthalide' was found to contain two hydroxyl groups. It can be formulated as a dihydroxynaphthacene quinone, and its production from ethylene diphthalide explained in the following manner.



Another method for the production of naphthacenequinone derivatives was introduced by Deichler and Weizmann (Ber. 1903, 36, 547) who condensed α-naphthol with phthalic acid in presence of concentrated sulphuric acid.



Naphthacenequinone $C_{18}H_{10}O_2$. By oxidising 6 grms. of dihydronaphthacene in 360 c.c. of glacial acetic acid with 9 grms. of chromic acid dissolved in 9 c.c. of water and 90 c.c. of glacial acetic acid. Long yellow needles, m.p. 294° (Gabriel and Leupold, Ber. 1898, 31, 1277).

1 - Chloronaphthacenequinone $C_{18}H_9ClO_2$. From hydroxynaphthacene quinone and phosphorus pentachloride, m.p. 254° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 118).

1 : 6-Dichloronaphthacenequinone $C_{18}H_8Cl_2O_2$. From dihydroxynaphthacene quinone and phosphorus pentachloride, m.p. 259°–260° (Gabriel and Leupold, Ber. 1898, 31, 1282).

Bromo-1-chloronaphthacenequinone $C_{18}H_8ClBrO_2$, m.p. 180° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 119).

Nitronaphthacenequinone $C_{18}H_9(NO_2)O_2$. By nitration of naphthacene quinone, m.p. 315° (Gabriel and Leupold, *l.c.* 1278).

Dinitronaphthacenequinone $C_{18}H_8(NO_2)_2O_2$. From dihydronaphthacene and nitric acid, m.p. 240° (*ibid.*).

1-Hydroxynaphthacenequinone $C_{18}H_9(OH)O_2$. Prepared by intimately mixing 50 grms. of phthalic acid, 44 grms. of α-naphthol and 50 grms. of boric acid, then adding 500 c.c. of 97 p.c. sulphuric acid and heating to 160°, maintaining the temperature for about 1 hour at 160°–165° until no further alteration in the red colouration is observed. The mixture is poured into water, the precipitate collected and dissolved in a boiling 10 p.c. solution of caustic potash and the potassium salt, which separates on cooling, dissolved in boiling water and decomposed by hydrochloric acid. Long reddish-yellow needles from nitrobenzene, m.p. 303°.

Acetyl derivative $C_{18}H_9(OCOCH_3)O_2$ (Deichler and Weizmann, Ber. 1903, 36, 550).

6-Chloro-1-hydroxynaphthacenequinone

$C_{18}H_8Cl(OH)O_2$,

m.p. 290°–293°. *Acetyl derivative*, m.p. 270°–273° (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 418).

7 : 10-Dichloro-1-hydroxynaphthacenequinone $C_{18}H_7Cl_2(OH)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 283).

7 : 8 : 9 : 10-Tetrachloro-1-hydroxynapthacenequinone $C_{18}H_5Cl_4(OH)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 287).

Bromo-1-hydroxynaphthacenequinone

$C_{18}H_8Br(OH)O_2$.

By brominating 1-hydroxynaphthoylbenzoic acid and condensing with sulphuric acid. With phosphorus pentachloride gives chlorobromonaphthacenequinone of m.p. 180° (Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 119).

6-Nitro-1-hydroxynaphthacenequinone

$C_{18}H_8(NO_2)(OH)O_2$.

By nitration of hydroxynaphthacene quinone, m.p. 274° (Deichler and Weizmann, Ber. 1903, 36, 2326).

Dinitro-1-hydroxynaphthacenequinone

$C_{18}H_7(NO_2)_2(OH)O_2$,

m.p. 260° (D. and W. *ibid.* 2327).

2 : 6 ?-Dinitro-1-hydroxynaphthacenequinone, m.p. 275°. *Acetyl derivative*, m.p. 276°–278° (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 419).

1 : 5-Dihydroxynaphthacenequinone

$C_{18}H_8(OH)_2O_2$.

From 1′ : 5′-dihydroxy-2-β-naphthoylbenzoic acid. Brick-red powder, sublimes below 300° (Bentley, Friedl and Weizmann, *ibid.* 1907, 91, 1593).

1 : Hydroxy-5 : methoxynaphthacenequinone (Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 425).

7 : 10-Dichloro-1 : 5-dihydroxynaphthacenequinone $C_{18}H_6Cl_2(OH)_2O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 284).

1 : 6-Dihydroxynaphthacenequinone

$C_{18}H_8(OH)_2O_2$.

75 grms. of crude ethylene phthalide are suspended in 250 c.c. of methyl alcohol, warmed on a water-bath at 60°, and mixed with a solution of 17 grms. of sodium in 300 c.c. of methyl alcohol. The mixture is boiled 20 or 30 minutes under reflux, filtered, and the residue washed with absolute alcohol. By boiling the black residue with 1 litre of water and filtering, a solution of the sodium salt of *bis*-diketohydrindene is obtained (yield of *bis*-diketohydrindene, 32·5 grms., m.p. 297°). The residue of *iso*-ethylenediphthalide and its sodium salt is repeatedly boiled with water and then with dilute hydrochloric acid. Yield 16·5 grms., m.p. 346°–347° (uncorr.) (Gabriel and Leupold, Ber. 1898, 31, 1161).

Liebermann and Flatau (*ibid.* 1901, 34, 2151) found that the potassium salt was formed when *tris*-diketohydrindene was boiled with a solution of two molecules of alkali. They give no melting-point.

Deichler and Weizmann (Ber. 1903, 36, 721) obtained the substance by heating 10 grms. of 1-hydroxynaphthacenequinone with 10 grms. of boric acid and 100 grms. of 96 p.c. sulphuric acid 3–4 hours at 230°; m.p. 300° (uncorr.).

Gabriel and Leupold consider the compound to be identical with the 'indenigo' obtained by the oxidation of diphthalylethane with hydrogen peroxide or potassium persulphate (V. Kaufmann, Ber. 1897, 30, 386; no melting-point given).

1 : 6-Dihydroxynaphthacene quinone forms red needles, the solution in concentrated sulphuric acid is deep red or yellow, according to strength, and fluoresces on addition of boric acid. The potassium salt is very sparingly soluble; the solution in boiling water is violet.

Dihydronaphthacene is obtained when 3 grms. of dihydroxynaphthacene quinone and 3 grms. of red phosphorus are intimately mixed, stirred with 22 c.c. of hydriodic acid (b.p. 127°) and heated for 3 to 4 hours in a sealed tube at 154°–157°. The residue is extracted with water and crystallised from 50 c.c. of benzene; the dihydronaphthacene melts at 206°–207° and distils about 400° (Gabriel and Leupold, Ber. 1898, 31, 1276).

1 : 6-Dihydroxynaphthacenequinone gives a *diacetyl* (m.p. 235°) and a *dibenzoyl* (m.p. 334°–339°) derivative (Gabriel and Leupold, Deichler and Weizmann).

7 : 10-Dichloro-1 : 6-dihydroxynaphthacenequinone $C_{18}H_6Cl_2(OH)_2O_2$ gives a diacetyl derivative of m.p. 265° (Harrop and Weizmann, Chem. Soc. Trans. 1909, 95, 283).

7 : 8 : 9 : 10-Tetrachloro-1 : 6-dihydroxynaphthacenequinone $C_{18}H_4Cl_4(OH)_2O_2$ (Harrop and Weizmann, *ibid.* 287).

Dinitro-1 : 6-dihydroxynaphthacenequinone $C_{18}H_6(NO_2)_2(OH)_2O_2$. By passing nitrous fumes into a sulphuric acid solution of the dihydroxy-compound. Gives a *diamino-dihydroxy-naphthacenequinone* on reduction (Deichler and Weizmann, Ber. 1903, 36, 2329).

1 : 7- or 1 : 10-Dihydroxynaphthacenequinone $C_{18}H_8(OH)_2O_2$. 1′-Hydroxy-3 (or 6)-methoxy-2-β-naphthoylbenzoic acid (m.p. 210°–215°) is obtained by the condensation of methoxyphthalic anhydride with α-naphthol, and then heated with concentrated sulphuric acid. Reddish-violet fluorescent solution in concentrated sulphuric acid; m.p. indefinite, 280°–300° (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 421).

1 : 8 or 1 : 9-Dihydroxynaphthacenequinone. By condensing 4-hydroxyphthalic acid with α-naphthol and heating the product with sulphuric acid. Does not melt by 330°. *Diacetyl derivative*, m.p. 227°–228°. 1-*Hydroxy*-8 or 9-*methoxy-naphthacenequinone* melts about 250° (Bentley, Friedl, Thomas and Weizmann, *ibid.* 422).

1 : 4 : 5-Trihydroxynaphthacenequinone ?

$C_{18}H_7(OH)_3O_2$

does not melt below 360°. The solutions in cold sodium carbonate and concentrated sulphuric acid are cornflower-blue in colour (Bentley, Friedl and Weizmann, *ibid.* 1907, 91, 1593).

Trihydroxynaphthacenequinones have also been prepared by fusing 1 : 6-dihydroxynaphthacenequinone with alkali (Deichler and Weizmann, Ber. 1903, 36, 725) and by alkaline fusion of the sulphonic acid obtained from 1 : 6-aminohydroxynaphthacene quinone (Bentley, Friedl, Thomas and Weizmann, Chem. Soc. Trans. 1907, 91, 417).

1-Aminonaphthacenequinone

$C_{18}H_9(NH_2)O_2$.

From hydroxynaphthacene quinone and ammonia; m.p. 290°–292° (*ibid.* 415).

1-Amino-6-hydroxynaphthacenequinone

$C_{18}H_8(NH_2)(OH)O_2$.

By reduction of the nitro compound (Deichler and Weizmann, Ber. 1903, 36, 2328; Orchardson and Weizmann, Chem. Soc. Trans. 1906, 89, 121; Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 417).

7 : 10 - Dichloro-1-hydroxy - 6 - aminonaphthacenequinone $C_{18}H_6Cl_2(OH)(NH_2)O_2$ (Harrop and Weizmann, *ibid.* 1909, 95, 284).

1-Anilino-6-hydroxynaphthacenequinone

$C_{18}H_8(NHC_6H_5)(OH)O_2$

and its *acetyl derivative* (Bentley, Friedl, Thomas and Weizmann, *ibid.* 1907, 91, 419).

2 ?-Nitro-6 ?-anilino-1-hydroxynaphthacenequinone $C_{18}H_7(NO_2)(NHC_6H_5)(OH)O_2$ (*ibid.* 420).

7 (or 10)-Chloro-10 (or 7)-anilino-1-hydroxynaphthacenequinone

$C_{18}H_7Cl(NHC_6H_5)(OH)O_2$

(Harrop and Weizmann, *ibid.* 1909, 95, 285).

1-Amino-6 : 8 (or 9)-dihydroxynaphthacenequinone $C_{18}H_7(NH_2)(OH)_2O_2$ (*ibid.* 423).

1 : 6-Dianilinonaphthacenequinone

$C_{18}H_8(NHC_6H_5)_2O_2$.

By the action of aniline on dichloronaphthacene quinone (Gabriel and Leupold, Ber. 1898, 31, 1283).

8 : 9-Dichloro-7 : 10-dianilino-1-hydroxynaphthacenequinone

$C_{18}H_5Cl_2(NHC_6H_5)_2(OH)O_2$

(Harrop and Weizmann, Chem. Soc. Trans. 1909, 95, 288).

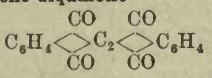
7 : 10-Dianilino-1 : 5-dihydroxynaphthacenequinone $C_{18}H_6(NHC_6H_5)_2(OH)_2O_2$ (*ibid.* 285).

8 : 9-Dichloro-7 : 10-dianilino-1 : 6-dihydroxynaphthacenequinone

$C_{18}H_4Cl_2(NHC_6H_5)_2(OH)_2O_2$

(*ibid.* 288).

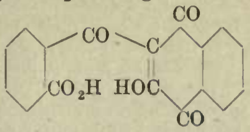
Naphthacene-diquinone



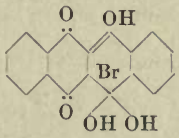
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_2\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$$

is obtained by the action of nitric acid on 1 : 6-dihydroxynaphthacene quinone. Sinters at 325°, m.p. 330°–333° (Gabriel and Leupold, Ber. 1898, 31, 1283).

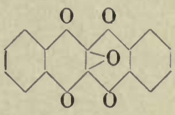
The action of halogens on naphthacene-diquinone has been examined by Voswinckel (Ber. 1905, 38, 4015). The colourless dichloride, $C_{18}H_8O_4Cl_2$, of m.p. 175°, gives the acid



when treated with soda. With bromine, trihydroxynaphthacenequinone bromide



m.p. 198°, is obtained, whilst bleaching powder gives an oxide



melting about 240°.

Voswinckel draws attention to the fact that several compounds which have been described at different times belong probably to the naphthacenequinone series (*e.g.* dibenzoylsuccinic dianhydride, L. Knorr and Scheidt, Annalen, 1896, 293, 74).

1 : 2-Chrysoquinone $C_{18}H_{10}O_2$. By oxidation of chrysene with chromic acid (Liebermann, Annalen, 1871, 158, 309; Graebe, Ber. 1874, 7, 784; Bamberger and Burgdorf. *ibid.* 1890, 23, 2437; Schmidt, J. pr. Chem. 1874, [ii.] 9, 284; Graebe and Hönigsberger, Annalen, 1900, 311, 262). Crystallises in needles from toluene and benzene or in plates from hot glacial acetic acid: m.p. (corr.) 239·5°. *Monooxime*, m.p. 160°–161° (Graebe and Hönigsberger).

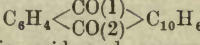
The reactions of chrysoquinone resemble those of phenanthraquinone. Derivatives have been described by Liebermann (*l.c.*); Adler (Ber. 1879, 12, 1892); Japp and Streatfeild (Chem. Soc. Trans, 1882, 41, 157) and Abegg (Ber. 1891, 24, 953).

2 : 8- or *amphi*-**Chrysoquinone.** By oxidising 2 : 8-dihydroxychrysene in boiling glacial acetic acid with lead peroxide. Reddish-yellow needles m.p. 288°–290°. *Compound*

$C_{18}H_{10}O_2{\cdot}NaHSO_3{\cdot}2H_2O$.

Oxidised by air in hot alcoholic suspension to 8-hydroxy-1 : 2 chrysoquinone, dark-red needles which decompose above 300°. Gives 8-hydroxy-1 : 2-chrysoquinone-1-phenylimine, m.p. 230°, on treatment with aniline (Beschke and Diehm, Annalen, 1911, 384, 173).

Naphthanthraquinone

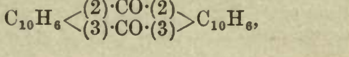


$C_6H_4\left\langle\begin{matrix}CO(1)\\CO(2)\end{matrix}\right\rangle C_{10}H_6$.

From naphthoyl-*o*-benzoic acid and concentrated sulphuric acid. Constitution, Gabriel and Colman (Ber. 1900, 33, 449). *Mononitro-derivatives*, &c. (R. Scholl, *ibid.* 1911, 44, 2370, 2992; Monatsh. 1912, 33, 507).

QUINONES $C_nH_{2n-32}O_2$.

Dinaphthanthraquinone



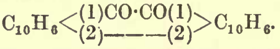
$$C_{10}H_6\left\langle\begin{matrix}(2){\cdot}CO{\cdot}(2)\\(3){\cdot}CO{\cdot}(3)\end{matrix}\right\rangle C_{10}H_6,$$

m.p. 388–389°. By oxidising tetrahydrodinaphthanthracene with anhydrous ferric chloride in glacial acetic acid solution. Flattish, yellow needles, soluble in concentrated sulphuric acid, the solution is blue by transmitted, crimson by reflected light (Mills and Mills, Chem. Soc. Trans. 1912, 101, 2206).

5:7:12:14 - **Dinaphthanthradiquinone** (Mills and Mills, *loc. cit.* p. 2200), m.p. 408°.

5 : 6 : 7 : 12 : 13 : 14 - **Dinaphthanthratriquinone** (Russig, J. pr. Chem. 1900, [ii.] 62, 30).

Picene-quinone $C_{22}H_{12}O_2$, or



$$C_{10}H_6<\begin{matrix}(1)CO\cdot CO(1)\\(2)\text{———}(2)\end{matrix}>C_{10}H_6.$$

By oxidation of picene, $C_{22}H_{14}$, with chromic acid in acetic acid solution (Burg, Ber. 1880, 13, 1836; Bamberger and Chattaway, Annalen, 1895, 284, 64). Red crystalline powder, sublimes (with partial decomposition) as red needles and leaflets. Distilled with soda-lime, picene and ββ-dinaphthyl are produced.

Crackene-quinone $C_{24}H_{16}O_2$, m.p. 208°. By oxidation of crackene with chromic acid in acetic acid solution (Klaudy and Fink, Monatsh. 1900, 21, 131).

QUINONE $C_nH_{2n-38}O_2$.

Quinone $C_{32}H_{26}O_2$, m.p. 180°. By oxidising the hydrocarbon $C_{32}H_{28}$ (Carnelly, Chem. Soc. Trans. 1880, 37, 713).

QUINONES $C_nH_{2n-40}O_2$.

Dibenzhydryl-*p*-benzoquinone $C_{32}H_{24}O_2$ has already been described.

INTERMEDIATE QUINONES.

Quinones have been described in which both carbonyl groups are members of one ring; it will have been noticed that the two carbonyl groups may belong to different rings; although parts of the same nucleus, as in the cases of *amphi*-naphthaquinone and *amphi*-chrysenequinone. A few other quinones of such type are known.

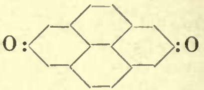
Fluorene-quinone $C_{13}H_8O_2$, is obtained together with diphenylene-ketone, $C_{13}H_8O$, when fluorene is oxidised by chromic acid in acetic acid solution; m.p. 181°–182° (Barbier, Ann. Chim. Phys. 1876, v. 7, 500). Possibly a substance obtained by Behr and van Dorp (Ber. 1874, 7, 399) in small quantity by distilling phenol with 5 parts of litharge is identical with fluorene quinone.

Methylenebiphenylquinones, melting at 280°–281° and 276°–278° respectively, have been described by Carnelly (Chem. Soc. Trans. 1880, 37, 709).

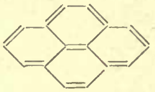
Pyrene-Quinone $C_{16}H_8O_2$. By the oxidation of pyrene with chromic acid (Graebe, Annalen, 1871, 158, 295; Bamberger and Philip, *ibid.* 1887, 240, 166; Goldschmiedt, Monatsh. 1883, 4, 310). A mixture of 10 grms. of pyrene, 15 grms. of potassium dichromate and 110 grms. of sulphuric acid diluted with 5 times its volume of water is heated until a reaction sets in. When apparently over, the mixture is boiled 1 hour longer. Then precipitate with water and digest with dilute sodium carbonate solution some hours at 50°. The residue is recrystallised from acetic acid until free from pyrene. Melts and decomposes about 282°. Soluble in sodium bisulphite solution. Reduced to dihydroxypyrene by boiling with zinc dust and ammonia.

Dibromo and *tribromo derivatives* (Goldschmiedt).

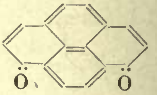
In place of the constitution



assigned to pyrene quinone by Bamberger and Philip (*l.c.* 158). Goldschmiedt considers that pyrene and its quinone should be represented by the respective formulæ

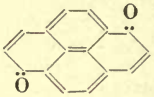


and



(Annalen, 1907, 351, 258).

Whilst Scholl and Seer consider it to have the constitution

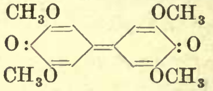


(Monatsh. 1912, 33, 1).

HETERONUCLEAR QUINONES.

DERIVATIVES OF DIPHENYL.

The earliest known quinone of the diphenyl series, coerulignone, had the constitution



assigned to it by Liebermann (Annalen, 1873, 169, 221; Ber. 1872, 5, 746; 1873, 6, 781; Liebermann and Flatau, *ibid.* 1897, 30, 234; Liebermann and Cybulski, *ibid.* 1898, 31, 615). The parent substance, diphenoquinone, was not isolated until 1905, despite the earlier efforts of Magatti (*ibid.* 1879, 12, 1863; 1880, 13, 224).

4 : 4′-**Diphenoquinone** $O : C_6H_4 : C_6H_4 : O$. Obtained by shaking 10 grms. of *p*-diphenol dissolved in 1 kilo. of ether for one day with 100 grms. of lead peroxide. Two varieties: these crystallise from benzene in thick crystals resembling chromic acid and brighter coloured fine needles respectively. Easily reduced to diphenol, even by phenylhydrazine at the ordinary temperature; liberates iodine from an acidified solution of potassium iodide (Willstätter and Kalb, Ber. 1905, 38, 1232).

Diphenoquinhydrone $C_{24}H_{18}O_4$ gives a cornflower-blue solution in concentrated sulphuric acid and yields a beautiful violet sodium salt.

Diphenoquinone-diimine

$$NH : C_6H_4 : C_6H_4 : NH.$$

By oxidising benzidine in indifferent solvents with silver oxide or lead peroxide the di-imine of diphenoquinone is probably first formed; it polymerises, however, to

$$NH_2C_6H_4\cdot C_6H_4\cdot N : N\cdot C_6H_4\cdot C_6H_4NH_2$$

(Willstätter and Kalb, Ber. 1905, 38, 1238; 1906, 39, 3474).

Diphenoquinone dimethyldiimonium platinichloride $C_{14}H_{16}N_2Cl_6Pt + H_2O$, forms beautiful golden brown prisms. It is obtained by addition of chloroplatinic acid to a solution of the green chloride $C_{14}H_{17}ON_2Cl$, obtained from a solution of dimethylbenzidine in dilute hydrochloric acid and excess of ferric chloride (Willstätter and Kalb, Ber. 1904, 37, 3774; compare Willstätter, *ibid.* 1908, 41, 3250).

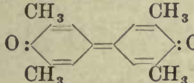
Diphenoquinone-tetramethyldiimonium bisulphate $HSO_4(CH_3)_2N{:}C_6H_4{:}C_6H_4{:}N(CH_3)_2SO_4H+2H_2O$ separates in red prisms, which appear blue or violet by reflected light, when excess of chlorine or nitrous acid is led into a solution of 1 grm. of tetramethylbenzidine in 10 c.c. of 30 p.c. sulphuric acid and 50 c.c. of 96 p.c. alcohol (Willstätter and Kalb, Ber. 1904, 37, 3768). The *chloride* is too deliquescent to analyse but the *platinichloride* $C_{16}H_{20}N_2Cl_6Pt+2H_2O$ and the *periodide* $C_{16}H_{20}N_2I_4$, have been isolated. Solutions of the salts are intensely orange-yellow; alkalies first give green solutions of a compound of meriquinonoïd type and decomposition then ensues. With sulphurous acid, tetramethylbenzidine monosulphonic acid is produced (compare Willstätter and Piccard, Ber. 1908, 41, 1466, 3250).

Diphenoquinone dichlorodiimine $C_{12}H_8N_2Cl_2$, chocolate brown amorphous powder, explodes at 135°, or red needles which explode at 155°–160° (Schlenk, Knorr and Keller, Annalen, 1908, 363, 313; 1909, 368, 271).

Resorcinol and halogens yield trihalogen substituted resorcinols; further action of halogen yields derivatives of diphenyl which are probably quinones of the 4 : 4′-series (Zincke and Schwabe, Ber. 1909, 42, 797).

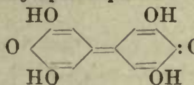
Orthodiphenol appears to be incapable of giving a quinone (Ber. 1905, 38, 1233 footnote); but Schlenk, Knorr and Keller (*l.c.*) have described the *dichlorodiimine* of the 2 : 4′-*quinone*, $ClN{:}C_6H_4{:}C_6H_4{:}NCl$, as a light brown amorphous powder which explodes on heating.

Tetramethyldiphenoquinone



By adding a solution of 1½–2 times the theoretical amount of chromic anhydride dissolved in strong acetic acid to a hot solution of *vic. m*-xylenol in 50 times its weight of glacial acetic acid. Dark red crystals, bluish reflex, m.p. 207°–217°, according to rapidity of heating. Yellowish-brown solution in concentrated sulphuric acid; oxidising agent (Auwers and von Markovitz, Ber. 1905, 38, 226).

Tetrahydroxydiphenoquinone



By oxidising an aqueous solution of hexahydroxydiphenyl with an alcoholic solution of iodine (Liebermann and Bung, Ber. 1876, 9, 1887). Microscopic blue needles, blue solution in alkalies. The necessary hexahydroxy-diphenyl is obtained from the reduction product of coerulignone by hydrolysis with hydrochloric acid (Liebermann, Annalen, 1873, 169, 239). The *dimethyl* and *trimethyl* ethers have been obtained by partial hydrolysis of coerulignone.

Tetramethoxydiphenoquinone (Cedriret or Coerulignone). $O{:}C_6H_2(OCH_3)_2{:}C_6H_2(OCH_3)_2{:}O$. By treating an acetic acid solution of pyrogallol-dimethyl ether (occurs in beech and birch tars) with potassium dichromate. The ether may also be oxidised by ferric chloride, chlorine, iodine or nitric acid (Hofmann, Ber. 1878, 11, 335). The production of coerulignone by addition of potassium dichromate to crude acetic acid obtained by distilling wood is easily explicable (Liebermann, Annalen, 1873, 169, 231). The coerulignone which separates on standing some days is dissolved in phenol (not above 30°) and precipitated by alcohol. Dark steel blue needles, insoluble in most organic solvents, soluble in concentrated sulphuric acid with cornflower-blue colour. By addition of water to the sulphuric acid solution, the *di-* and *tri-methyl ethers* of diphenoquinone are precipitated. Decomposed by alkalies, reducing agents furnish hydrocoerulignone (tetramethoxy diphenol).

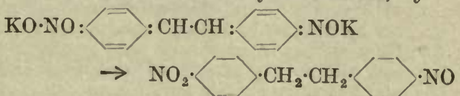
Coerulignone yields dyes when heated with aromatic amines; two molecular proportions of the latter are employed (Akt. Ges. Anilin-F., D. R. P. 94503, 1897). As an example, 10 parts of coerulignone are heated with 8 parts of *p*-toluidine and 120 parts of glacial acetic acid. The reaction begins at once, the solution becoming a beautiful blue; the reaction is finished in 15 minutes. Most of the dyestuff can be filtered off from the cold solution, the remainder may be recovered by precipitation with water. Various amines as well as their amino-carboxylic and sulphonic acids, may be employed. Friedländer (Fortschritte der Theerfarbenfabrikation, iv. 1060) states that the quinone-anilide dyes obtained in this manner are too unstable for practical application. For the action of amines or coerulignone compare Liebermann (Ber. 1897, 30, 234, 3137; 1898, 31, 615).

Tetraethoxydiphenoquinone or ethyl coerulignone, $C_{20}H_{24}O_6$ (Hofmann, Ber. 1878, 11, 801). A compound $C_{20}H_{24}O_6HNO_3$ separates as purple needles on leading nitrous fumes into an ethereal solution of pyrogallol diethyl ether. Hydrolyses immediately by water (Weselsky and Benedikt, Monatsh. 1881, 2, 215).

Derivatives of Stilbene.

Stilbenequinone $O{:}C_6H_4{:}CH{\cdot}CH{:}C_6H_4{:}O$. Obtained by the action of ferric chloride on *pp′*-dihydroxystilbene in presence of calcium carbonate (Zincke and Fries, Annalen, 1902, 325, 19; Zincke and Münch, *ibid.* 1904, 335, 157); or by shaking a suspension of 2 grms. of dihydroxystilbene in 500 c.c. ether for several hours with 25 grms. of lead peroxide. Extracted by benzene from its mixture with the lead oxides; m.p. 284°. Reduced to dihydroxystilbene by phenylhydrazine (Willstätter and Benz, Ber. 1906, 39, 3490; *see* also Zincke and Münch, *l.c.*).

Nitroximes and *oximes* of stilbenequinone exist as alkaline salts; the free compounds pass over, however, into dibenzyl derivatives, *e.g.*



(A. G. Green, Ber. 1897, 30, 3097; Chem. Soc.

Trans. 1904, 85, 1424, 1432; 1907, 91, 2076; 1908, 93, 1721).

Tetrabromostilbenequinone

$O : C_6H_2Br_2 : CH{\cdot}CH : C_6H_2Br_2 : O.$

Dihydroxystilbene and bromine yield tetrabromodi-*p*-hydroxydibenzyl ψ-bromide (tetrabromo-di-*p*-hydroxystilbene dibromide), m.p. 265°, which, boiled with acetone, gives the quinone. Also obtained by oxidising 3 : 5 : 3′ : 5′-tetrabromo-4 : 4′-dihydroxystilbene with nitric acid. Red powder or steel blue needles from nitrobenzene, changes to a pale yellow at 300° (Zincke and Fries, *l.c.*).

2 : 5 : 2′ : 5′-Tetrabromo-3 : 3′-dimethylthiolstilbene-4 : 4′-quinone

$O{:}C_6HBr_2(SCH_3){:}CH{\cdot}CH{:}C_6HBr_2(SCH_3){:}O.$

By the action of solid sodium acetate on an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol ψ-bromide. Deep black powder, m.p. 240° with decomposition (Zincke and Kempf, Ber. 1911, 44, 413; Zincke, Frohneberg and Kempf, Annalen, 1911, 381, 28).

DERIVATIVES OF AZOBENZENE.

Azobenzenequinone, or quinone azine

$O : C_6H_4 : N{\cdot}N : C_6H_4 : O.$

By shaking a solution of 5 grms. of hydrated *p*-azophenol $HO{\cdot}C_6H_4{\cdot}N : N{\cdot}C_6H_4{\cdot}OH$, dissolved in 1 litre of ether with silver oxide (obtained from 15 grms. of silver nitrate) and 10 grms. of ignited sodium sulphate. About 2 grms. of the quinone-azine may be obtained by evaporating the ether, the yield can be raised to 90 p.c. of the theoretical by boiling out the silver mud with three portions each of 100 c.c. of chloroform and evaporating the solvent. Purified by recrystallisation from ethyl acetate (Willstätter and Benz, Ber. 1906, 39, 3486). Crystallises either as dark orange-red prisms, giving a brick-red powder, or in dark yellow leaflets, powder yellow. Explodes at 158°. The solutions are deeper coloured than those of azophenol. Liberates iodine from acidified potassium iodide. Partial reduction gives the *quinhydrone*

$C_{24}H_{18}O_4N_4,$

m.p. 181°–182°, the same compound is obtained by mixing equimolecular quantities of the quinone-azine and azophenol in ethereal solution. Stronger reducing agents (*e.g.* aluminium amalgam, zinc dust and water, stannous chloride and hydrochloric acid) give an azophenol not identical with the azophenol from which the quinone-azine was prepared (Willstätter and Benz, Ber. 1906, 39, 3492).

ADDITION COMPOUNDS OF QUINONES.

(MERIQUINONOÏD COMPOUNDS).

A large number of substances are known in which quinonoïd and benzenoïd compounds have entered into a somewhat loose combination. The earliest-known member of this group was *quinhydrone*, a strongly coloured equimolecular compound of quinone and quinol discovered by Wöhler in 1844 (Annalen, 51, 153). The term quinhydrone is now used generically for the addition products of quinones and phenols, but since similar addition products of quinone-diimonium salts with aromatic diamines are also known which are likewise intensely coloured, Willstätter has introduced the term *meriquinonoïd* to include all compounds formed by addition of quinonoïd and benzenoïd molecules (Willstätter and Piccard, Ber. 1908, 41, 1458).

The relationships between quinone, quinol, and quinhydrone were obscured for some time, owing to the last being produced as an intermediate compound during the conversion of quinone into chloroquinol by addition of hydrogen chloride (Staedeler, Annalen, 1849, 69, 308). Quinhydrone is, however, undoubtedly an addition product, for besides the methods of preparation used by Wöhler, viz. the incomplete oxidation of quinol or the incomplete reduction of quinone, it is also formed by the combination of quinone and quinol $C_6H_4O_2+C_6H_4(OH)_2=C_{12}H_{10}O_4$ and may be resolved into its constituents by boiling with water, the quinone volatising and the quinol remaining in solution. Quinone generally combines with two molecules of a monatomic phenol, or with one of a diatomic phenol, although Wichelhaus at one time held the view that quinhydrone itself contained two molecules of quinol to one of quinone (Ber. 1872, 5, 849; 1879, 12, 1500). This idea was negatived by the work of Liebermann (*ibid.* 1877, 10, 1614), Nietzki (*ibid.* 2003; Annalen, 1882, 215, 125) and Hesse (*ibid.* 1880, 200, 232).

The quinhydrones and other meriquinonoïd compounds in common with many deeply coloured inorganic substances (*e.g.* sulphur sesquioxide, Prussian blue, &c.), have a constituent present in two distinct stages of oxidation. In the meriquinonoïd compounds, a dynamical equilibrium is supposed to exist between two or three molecules or benzene nucleï, similar to the intramolecular dynamical equilibrium, which, under the name of *isorrhopesis*, has been employed by Baly to furnish an explanation of the absorption of various carbonyl-compounds (*see* Chem. Soc. Trans. 1904, 85, 1029; 1905, 87, 766; 1332, 1347, 1355; 1906, 89, 502, 514, 966, 982; 1907, 91, 1572; 1908, 93, 1747, 1806, 1902; 1909, 95, 144, 1096).

Whilst the quinhydrones, are formed by the addition of quinones and phenols, the formation of quinhydrone as an intermediate product when hydrogen chloride is passed into a solution of quinone still has to be explained, especially in view of the fact that with a sufficient amount of hydrogen chloride a practically quantitative yield of chloroquinol is obtained. Wichelhaus, finding that quinone oxidises substituted quinols to substituted quinones whilst it is itself reduced to quinol, offered as an explanation that quinol liberates chlorine from hydrogen chloride which then acts upon quinol.

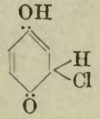
$$C_6H_4O_2+2HCl=C_6H_4(OH)_2+Cl_2$$
$$C_6H_4(OH)_2+Cl_2=C_6H_3Cl(OH)_2+HCl.$$

The production of chlorine appears improbable. Thiele's theory (Annalen, 1899, 306, 133) obviates this difficulty, but does not account for the intermediate production of quinhydrone (*see* Michael, J. pr. Chem. 1903, 68, 509; 1909, 79, 423; Posner, Annalen, 1904, 336, 109). Michael and Cobb (J. pr. Chem. 1910, 82, 298) assume the production of a complex

$$2C_6H_4O\ +HCl,$$

which decomposes giving nascent chlorine, the latter acts as a substituting agent on quinone instead of being directly added.

Posner supposes an addition product



is first formed and is then oxidised to chloroquinone which with quinol gives a substituted quinhydrone. The latter compound and hydrogen chloride give two molecules of chloroquinol (J. pr. Chem. 1911, ii. 83, 478).

Schmidlin (Ber. 1911, 44, 1700). considers Thiele's theory sufficient. The first action of hydrogen chloride is to furnish chloroquinol, which establishes an equilibrium with quinone, quinol and chloroquinone in the following sense:

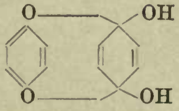
$$O{:}C_6H_4{:}O + HO{\cdot}C_6H_3Cl{\cdot}OH \rightleftharpoons HO{\cdot}C_6H_4{\cdot}OH + O{:}C_6H_3Cl{:}O.$$

This view is supported by the observations of Wichelhaus (Ber. 1879, 12, 1503), Biltris (Bull. Acad. roy. Belge, 1898, iii. 35, 44), and Valeur (Ann. Chim. Phys. 1900, vii. 21, 551) and explains the separation of non-substituted quinhydrone on adding hydrogen chloride to a solution of quinone in insufficient amount to effect complete conversion into chloroquinol. The solution will contain an equilibrium mixture of two quinones and two quinols, from which the least soluble (the unsubstituted) quinhydrone separates.

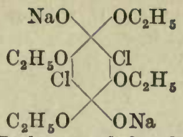
The observation of Ling and Baker (Chem. Soc. Trans. 1893, 63, 1314) that each of the two chloroquinhydrones (m.p. 138°–142° and 132°–133° respectively) give the sparingly soluble non-substituted quinhydrone and the more soluble dichloroquinhydrone on boiling with petroleum ether, is also easily explained, the quinhydrones being largely dissociated into their constituents in solution.

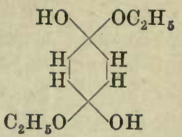
The quinhydrones and other meriquinonoïd compounds result from direct addition of quinonoïd and benzenoïd substances, and the question of the manner in which the two kinds of molecules are linked requires consideration.

In accordance with the peroxide formula for quinone, Graebe (Annalen, 1868, 146, 61) formulated quinhydrone as $HO{\cdot}C_6H_4{\cdot}O{\cdot}O{\cdot}C_6H_4{\cdot}OH$. A corresponding formula based on the diketonic formula for quinone is



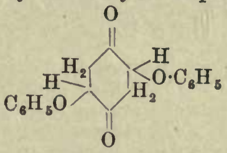
(C. Loring Jackson and Oenslager, Ber. 1895, 28, 1614). though it might be objected that a compound of such a constitution would hardly show selective absorption in the visible spectrum, whilst quinhydrone is actually a strongly-coloured substance. Jackson and Oenslager started out from the fact that dichlorodiethoxyquinone combines with two molecules of sodium ethoxide (Jackson and Grindley, Proc. Amer. Acad. 1894, 30, 409) and assumed that the salt was of hemiacetal type and corresponded to phenoquinone, the compound produced by the union of one molecule of quinone with two molecules of phenol.



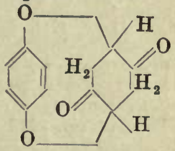


Jackson and Oenslager point out that their theory requires the union of one molecule of quinone with one molecule of a dihydric phenol such as quinol or resorcinol or with two molecules of phenol or the monomethyl ether of quinol, whilst the dimethyl ether of quinol should not react. The facts agree with these requirements except that Schlenk and Knorr have recently prepared an addition product of one molecule of dimethyl quinol ether with one molecule of quinone, and the production of diacetylquinol and quinone from quinhydrone and acetic anhydride (Hesse, Annalen, 1880, 200, 249), which Nietzki regarded as a proof of the absence of hydroxyl groups, is considered by Jackson and Oenslager to be a further argument in favour of their formula.

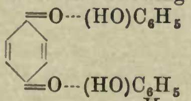
What may be designated as a 'phenol-ether' formula has been advocated by A. Valeur (Thèse, Paris, 1900; Gauthier-Villars, Ann. Chim. Phys. 1900, [vii.] 21, 546) and Th. Posner (Annalen, 1904, 336, 85); thus phenoquinone and quinhydrone may be respectively represented as

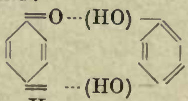


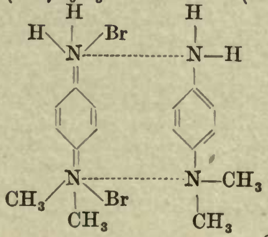
and



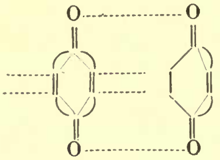
Willstätter and Piccard (Ber. 1908, 41, 1458) point out that none of these formulæ takes into account the deep colour and the easy dissociability of the quinhydrones (compare H. A. Torrey and H. Hardenbergh, Amer. Chem. J. 1905, 33, 167), and having discovered that the salts of bases obtained by Wurster by the oxidation of *p*-diamines (Ber. 1879, 12, 1803, 1807, 2071; 1886, 19, 3195, 3217) were only half quinonoïd, decided that the quinhydrones and Wurster's compounds belong to one category, residual affinity effecting a loose combination between the quinone or quinonoïd salt and the phenol or aromatic base. Quinhydrone is largely dissociated in aqueous solution. For quinone × quinol/quinhydrone K = 0·23 at 25° (Luther and Leubner, J. pr. Chem. 1912, [ii.] 85, 314). Phenoquinone, quinhydrone and Wurster's red (the product of the action of bromine on dimethyl-*p*-phenylenediamine) are then formulated in the following manner:





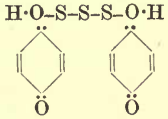


A somewhat similar idea is to be found in the formulation of quinhydrone as

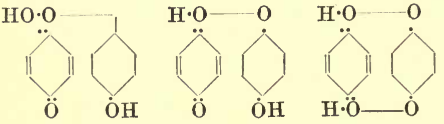


(G. Urban, Monatsh. 1907, 28, 299); Willstätter and Piccard (*l.c.*) 1464, footnote, point out that this does not take into account the salt formation of the quinhydrones.

M. M. Richter, who formulates the addition product of hydrogen persulphide and quinone as



thinks the quinhydrones are also oxonium compounds. Three oxonium formulæ



are possible for ordinary quinhydrone of which the second is preferred (Ber. 1910, 43, 3603). This view does not commend itself to Angelo Knorr (*ibid.* 1911, 44, 1503). The true imonium compound obtained from quinone-diimine and *p*-nitrophenol (m.p. 59°) is yellow, *i.e.* has not the marked colour associated with quinhydrones.

The meriquinonoid compounds obtained from bases were frequently mistaken for the quinonoid substances themselves.

Jackson and Calhane acted on *p*-phenylenediamine and its dibromo-derivative with bromine, obtaining deeply coloured salts which they considered were compounds of the diimines

$$C_6H_4(:NH)_2 \text{ and } C_6H_2Br_2(:NH)_2$$

(Ber. 1902, 35, 2495). Subsequently it was found that quinone-imine and quinone-diimine were colourless substances and gave colourless salts if in a state of purity (Willstätter and Pfannenstiehl, Ber. 1904, 37, 4606). Kehrmann suggested that many of the deeply coloured oxidation products obtained from simple amines might be of quinhydrone type (*ibid.* 1905, 38, 3777). A careful examination by Willstätter and Piccard (*ibid.* 1908, 41, 1458) of the oxidation products obtainable from dimethyl-*p*-phenylene diamine showed that whilst the completely quinonoid nitrate

$$HNO_3{\cdot}HN:C_6H_4:N(CH_3)_2NO_3$$

was colourless, the coloured salts obtained by Wurster (Ber. 1879, 12, 1803, 1807, 2071) and considered by Bernthsen (Annalen, 1885, 230, 162; 1889. 251, 11, 49, 82) to be wholly quinonoïd, are actually of meriquinonoïd type. Wurster's red must be considered as an addition product

$$BrNH_2:C_6H_4:N(CH_3)_2Br+NH_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$$

Kehrmann (Ber. 1908, 41, 2340), and Schlenk and Knorr both draw attention to the fact that quinhydrones are dissociated into their constituents in solution, but Wurster's red is not. Evidently the firmness of union of quinonoïd and benzenoid molecules varies in degree (Willstätter and Piccard, Ber. 1909, 42, 1902).

Jean Piccard (Annalen, 1911, 381, 351) has shown that the meriquinonediimonium salts

$$NH_2Br:C_6H_4:NH_2Br+NH_2{\cdot}C_6H_4{\cdot}NH_2$$

exist in two modifications, α and β. The α-compounds are formed preferably in presence of alcohol; the β-salts, which are polymers and more strongly coloured, at low temperatures, in presence of water. The β-form is usually the more stable.

Some of the addition products formed by quinones and quinonoïd compounds are given in the following list. The figures in brackets refer to the number of molecules of reacting substances, *e.g.*:—

(3) 1:4-$C_6H_4O_2$+(4)1:2:3 $C_6H_3(OH)_3$, m.p. 78°, Siegmund,

means that Siegmund has prepared an addition product of 3 molecules of *p*-benzoquinone with 4 molecules of pyrogallol which melts at 78°.

(1)1:4-$C_6H_4O_2$+(2)C_6H_5OH, m.p. 71°, Wichelhaus.
(1)1:4-$C_6H_4O_2$+(2)1:4-$C_6H_4(OCH_3)(OH)$
(1)1:4-$C_6H_4O_2$+(1)1:3-$C_6H_4(OH)_2$, m.p. 90°, Nietzki.
(1)1:4-$C_6H_4O_2$+(1)1:4-$C_6H_4(OH)_2$, m.p. 171°, Wöhler.
(1)1:4-$C_6H_4O_2$+(1)1:4-$C_6H_4(OCH_3)_2$, Schlenk and Knorr.
(1)1:4-$C_6H_4O_2$+(1)2:1:4-$C_6H_3Cl(OH)_2$, m.p. 145°, Ling and Baker.
(3)1:4-$C_6H_4O_2$+(4)1:2:3-$C_6H_3(OH)_3$, m.p. 78°, Siegmund.
(3)1:4-$C_6H_4O_2$+(4)1:2:4-$C_6H_3(OH)_3$, m.p. 164°, Siegmund.
(3)1:4-$C_6H_4O_2$+(2)1:3:5-$C_6H_3(OH)_3$, m.p. 103°, Siegmund.
(1)1:4-$C_6H_4O_2$+(1)2:3-$C_{10}H_6(OH)_2$, m.p. 78°–80°, Siegmund.
(5)1:4-$C_6H_4O_2$+(2)1:4-$C_6H_4(NH_2)_2$, m.p. 83°, Schlenk and Knorr.
(1)1:4-$C_6H_4O_2$+(1)$CH_2(C_6H_4{\cdot}NH_2)_2$, m.p. 72°–73°, Siegmund.
(1)1:4-$C_6H_4O_2$+(1)$C_2H_2(C_6H_4{\cdot}NH_2)_2$, m.p. 130°, Siegmund.
(1)1:4-$C_6H_4O_2$+(2)1:4-$NH_2{\cdot}C_6H_4{\cdot}CO_2CH_3$, m.p. 83°, Siegmund.
(1)2:1:4-$C_6H_3ClO_2$+(1)1:4-$C_6H_4(OH)_2$, m.p. about 130°, Ling and Baker.
(1)2:1:4-$C_6H_3ClO_2$+(1)2:1:4-$C_6H_3Cl(OH)_2$, m.p. 93°–94°, Wöhler; Ling and Baker.
(1)2:5:1:4-$C_6H_2Cl_2O_2$+(1)2:5:1:4-$C_6H_2Cl_2(OH)_2$, m.p. 140°–145°, Ling and Baker.
(1)2:6:1:4-$C_6H_2Cl_2O_2$+(1)2:6:1:4-$C_6H_2Cl_2(OH)_2$, m.p. 130°, Ling and Baker.
(1)2:5:1:4-$C_6H_2Cl_2O_2$+(1)2:5:1:4-$C_6H_2Br_2(OH)_2$, m.p. 130°–135°, Ling and Baker.
(1)2:3:5:1:4-$C_6HCl_3O_2$+(1)2:3:5:1:4-$C_6HCl_3(OH)_2$, m.p. 109°–110°, Ling and Baker.
(1)2:3:5:6:1:4-$C_6Cl_4O_2$+(1)2:3:5:6:1:4-$C_6Cl_4(OH)_2$, m.p. 160°, Staedeler; Loring Jackson.
(1)*p*-$C_6Cl_4O_2$+(1)1:4-$C_6H_4(NH_2)_2$, Schlenk and Knorr.
(1)*p*-$C_6Cl_4O_2$+(1)1:4-$C_6H_4[N(CH_3)_2]_2$, m.p. 80°, Schlenk and Knorr.

$(1)p\text{-}C_6Cl_4O_2+(1)(CH_3)_2N\cdot C_6H_4\cdot C_6H_4\cdot N(CH_3)_2$, Schlenk and Knorr.

$(1)p\text{-}C_6Cl_4O_2+(1)NH_2\cdot C_6H_2Cl(CH_3)\cdot C_6H_2Cl(CH_3)\cdot NH_2$, Schlenk and Knorr.

$(1)p\text{-}C_6Cl_4O_2+(1)NH_2\cdot C_6H_2Br(CH_3)\cdot C_6H_2Br(CH_3)\cdot NH_2$, m.p. 225–228°, Schlenk and Knorr.

$(1)2:1:4\text{-}C_6H_3BrO_2+(1)2:1:4\text{-}C_6H_3Br(OH)_2$, m.p. 98°, Ling and Baker.

$(1)2:5:1:4\text{-}C_6H_2Br_2O_2+(1)2:5:1:4\text{-}C_6H_2Br_2(OH)_2$, m.p. 145°–150°, Ling and Baker.

$(1)2:5:1:4\text{-}C_6H_2Br_2O_2+(1)2:5:1:4\text{-}C_6H_2Cl_2(OH)_2$, m.p. 135°–140°, Ling and Baker.

$(1)p\text{-}C_6Br_4O_2+(1)(CH_3)_2N\cdot C_6H_4\cdot C_6H_4\cdot N(CH_3)_2$, Schlenk and Knorr.

$(1)p\text{-}C_6Br_4O_2+(1)NH_2\cdot C_6H_2Br(CH_3)\cdot C_6H_2Br(CH_3)\cdot NH_2\cdot$, m.p. 190°, Schlenk and Knorr.

$(1)2:1:4\text{-}C_6H_3(OH)O_2+(1)1:2:4\text{-}C_6H_3(OH)_3$, Barth and Schreder.

$(1)2:1:4\text{-}C_6H_3(CH_3)O_2+(1)2:1:4\text{-}C_6H_3(CH_3)(OH)_2\cdot$, m.p. 52°, Nietzki.

$(1)1:4:2:5\text{-}C_6H_2(CH_3)(C_3H_7)O_2+(1)1:4:2:5\text{-}C_6H_2(CH_3)(C_3H_7)(OH)_2$, Liebermann.

$(1)O:C_6H_4:C_6H_4:O+(1)HO\cdot C_6H_4\cdot C_6H_4\cdot OH$, Willstätter and Kalb.

$(1)1:4\text{-}C_6H_4(:NH)_2+(1)NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, m.p. 128°–145°, Schlenk and Knorr.

$(1)1:4\text{-}C_6H_4O(:NCl)+(1)1:4\text{-}C_6H_4(OH)_2$, expl. p. 119°, A. Knorr.

$(1)1:4\text{-}C_6H_4(:NCl)_2+(1)1:4\text{-}C_6H_4(OH)_2$ expl. p. 129°–130°, A. Knorr.

$(1)1:4\text{-}C_6H_4(:NCl)_2+(2)NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, expl. p. 121°, A. Knorr.

$(1)1:4\text{-}BrNH_2:C_6H_4:N(CH_3)_2Br+(1)1:4\text{-}NH_2\cdot C_6H_4\cdot N(CH_3)_2$, Willstätter and Piccard.

$(1)HSO_4\cdot N(CH_3)_2:C_6H_4:N(CH_3)_2SO_4H+(2)1:4\text{-}C_6H_4[N(CH_3)_2]_2,H_2SO_4$, Willstätter and Piccard.

$(1)NH:C_6H_4:C_6H_4:NH+(4)NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2+(4)H_2CrO_4$, Willstätter and Piccard.

$(1)NH:C_6H_4:C_6H_4:NH+(3)NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2+(5)H_2CrO_4$, Willstätter and Piccard.

$(1)Cl(CH_3)_2N:C_6H_4:C_6H_4:N(CH_3)_2Cl+(1)(CH_3)_2N\cdot C_6H_4\cdot C_6H_4\cdot N(CH_3)_2+(6)H_2O$, Willstätter and Piccard.

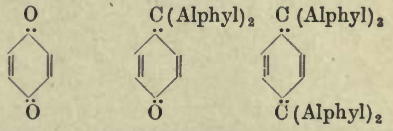
$(1)NH:C_6H_2(CH_3)Cl:C_6H_2(CH_3)Cl:NH+(1)NH_2.C_6H_2(CH_3)Cl\cdot C_6H_2(CH_3)Cl\cdot NH_2+(2)HCl$, Schlenk and Knorr.

Neither the above list of meriquinonoïd compounds nor the subjoined list of references pretends to be exhaustive. Some idea will be gained, however, of the types of substances which form meriquinonoïd compounds and the molecular proportions in which combination takes place.

Barth and Schreder, Monatsh. 1884, 5, 595; T. H. Clark, Amer. Chem. J. 1892, 14, 574; Graebe, Annalen, 1868, 146, 27; Haack, Ber. 1909, 42, 4595; Hesse, Annalen, 1880, 200, 248; C. L. Jackson and Carleton, Amer. Chem. J. 1908, 39, 493; Klinger and Standke, Ber. 1891, 24, 1340; Angelo Knorr, *ibid.* 1911, 44, 1503; Liebermann, *ibid.* 1877, 10, 1615; Ling and Baker, Chem. Soc. Trans. 1893, 63, 1314; W. Madelung, Ber. 1911, 44, 626; K. H. Meyer, *ibid.* 1910, 43, 157; Nietzki, Annalen, 1882, 215, 130; Ber. 1879, 12, 1982; Piccard, Annalen. 1911, 381. 351; Ber. 1911, 44, 959; M. M. Richter, *ibid.* 1910, 43, 3603; 1911, 44, 3466; Schlenk and Knorr, Annalen, 1908, 363, 313; 1909, 368, 271; W. Siegmund, Monatsh. 1908, 29, 1087; J. pr. Chem. 1910, ii. 82, 409; 1911, ii. 83, 553; Staedeler, Annalen, 1849, 69, 308; Urban, Monatsh. 1907, 28, 2399; Wichelhaus, Ber. 1872, 5, 248, 846; 1879, 12, 1500; Willstätter, *ibid.* 1905, 38, 1232; 1906, 39, 3474; 1908, 41, 1458, 3245; 1909, 42, 1909, 4143; Wöhler, Annalen, 1844, 51, 153: Woskresensky, J. pr. Chem. 1839, i. 18, 419; Zincke and Muhlhausen, Ber. 1905, 38, 756; C. L. Jackson and Bolton, Ber. 1912, 45, 871.

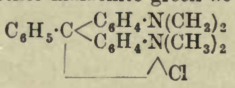
QUINONOÏD COMPOUNDS.

The term quinones is restricted to substances containing two carbonyl groups; in addition there are a large number of compounds in which the same arrangement of linkages exists, but the oxygen of the carbonyl group is replaced by other atoms or groups. Examples have already been seen in the imines, arylimines, chloroimines, and oximes of the quinones. These compounds have been described in connection with the quinones to which they correspond, as they are generally obtainable directly from the quinones or are converted into them by more or less easy means. In the cases where divalent carbon radicles replace the oxygen of the carbonyl groups there is the same formal relationship, *e.g.*

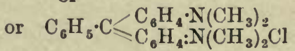


and the 'quinonoid' structure is evident, but generally such compounds are not directly convertible into the corresponding quinones.

Quinonoid structure is usually assumed to exist in the case of the organic dyestuffs; thus whether malachite green be written as

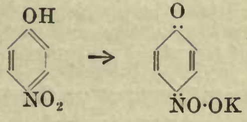


$$C_6H_5\cdot C{<}\begin{matrix}C_6H_4\cdot N(CH_2)_2\\ C_6H_4\cdot N(CH_3)_2\end{matrix}\ Cl$$



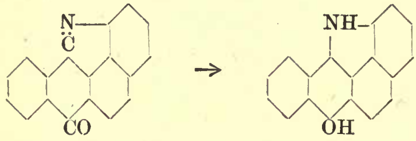
or $$C_6H_5\cdot C\begin{matrix}\diagup C_6H_4\cdot N(CH_3)_2\\ \diagdown\!\!\diagdown C_6H_4:N(CH_3)_2Cl\end{matrix}$$

the constitution must be regarded as quinonoid, the first formula corresponding to the peroxide formula, the second to the diketone formula of *p*-benzoquinone. A discussion of the constitution of dyestuffs is given in the article on CHROMOPHORES (*q.v.*), and it is mentioned there that many chemists assume that a rearrangement of linkages takes place when *p*-nitrophenol and allied substances form salts or ionise, the benzenoid giving place to the quinonoïd configuration.



Many quinonoïd compounds exhibit the same additive capacity for hydrogen, hydrogen chloride, &c., as the quinones themselves. in the case of the dyestuffs, however, the corresponding benzenoïd leuco-compounds oxidise spontaneously and furnish the corresponding quinonoïd dyestuffs. It may be noted that marked differences in ease of oxidisability exist, a leuco-compound corresponding to an *o*-quinonoïd dyestuff being far more readily oxidised than one from which a *p*-quinonoïd dyestuff is formed (Green, Chem. Soc. Proc. 1896, 12, 226).

Conversely it is found that quinones vary greatly in their oxidising power. Willstätter and Parnas (Ber. 1907, 40, 1406) show that whereas 2 : 6-(*amphi*-)naphthaquinone shares the strong oxidising properties of *p*-benzoquinone, 1 : 2-(*ortho*-)naphthaquinone shows these on a reduced scale, 1 : 4-(*para*-)naphthaquinone is a feeble oxidising agent, whilst properties of this nature are entirely absent in the case of anthraquinone. Possibly in the last case the explanation is to be found in the fact that the two carbonyl groups link up two real benzene nucleï. Quinonoïd compounds sometimes act as oxidising agents, phenylhydrazine reduces *p*-benzoquinone with evolution of nitrogen at the ordinary temperature; at a higher temperature it reduces aniline black (Willstätter and Cramer, Ber. 1910, 43, 2976), whilst 2 : 9-N-indoloanthrone is reduced by phenylhydrazine at the ordinary temperature (R. Scholl, Ber. 1911, 44, 2370).



The quinonoïd compounds not so far considered are those of such types as

$>C:C_6H_4:O$(or $:NR$ and $:NR_2Cl$ and $>C:C_6H_4:C<$

In the first category are many classes of dyestuffs, and reference should be made to the article dealing with triphenylmethane colouring matters. These substances can be considered as derived from quinomethane or its imine

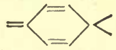
$$CH_2:C_6H_4:O \qquad CH_2:C_6H_4:NH$$

by replacement of hydrogen atoms by various groups. To diphenylquinomethane

$$(C_6H_5)_2C:C_6H_4:O$$

Baeyer has given the name *fuchsone* which lends itself easily to derivatives. Thus pararosaniline becomes diaminodiphenylfuchsonimonium chloride. The coloured quinonoïd hydrocarbons are derivatives of quinodimethane, $CH_2:C_6H_4:CH_2$, and an account of them is given below.

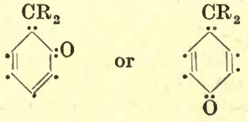
Besides truly quinonoid compounds a number of substances of hemiquinonoid character, possessing the grouping



are known (*e.g.* the pseudoquinols), which also frequently show a tendency to pass into substances of benzenoid configuration.

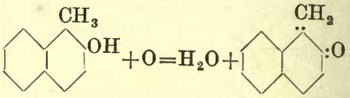
Methylene-Quinones or Quino-methanes.

These compounds contain the groupings

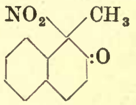


The simplest members of the series, the methylene benzoquinones $CH_2 : C_6H_4 : O$, are unknown, but many derivatives, substituted either in the methylene group or in the quinonoïd nucleus, have been obtained. Substances of this class have been prepared by the following methods :

1. By oxidation of *o*-methyl substituted naphthols. Fries and Hübner (Ber. 1906, 39, 446) obtained β-naphthoquino-1-methane by dissolving 4 grms. of 1-methyl-2-naphthol in 60 c.c. of glacial acetic acid and adding in the course of 1 hour, 12 grms. of sodium nitrite. After 8 hours, the solution was poured into water, the precipitate ground with a little glacial acetic acid, dried on porous earthenware and crystallised from petroleum spirit. Yellow needles, m.p. 132°



By using nitrous fumes and a solution of the methyl-naphthol in dry ether, a quinitrol



which decomposes and evolves nitric oxide at 140° may be obtained. Derived from this is the ψ-quinol $O:C_{10}O_6<^{CH_3}_{OH}$, m.p. 83°. Occasionally the oxidation may be effected by bromine without intermediate formation of a ψ-bromide. Zincke and Walter (Annalen, 1904, 334, 367) obtained benzylidene-2 : 6-dibromoquinone (dibromoquinophenylmethane) by heating bromine with dibromohydroxydiphenyl methane to 100° in carbon tetrachloride solution

$$C_6H_5\cdot CH_2\cdot C_6H_2Br_2OH + Br_2$$
$$= 2HBr + C_6H_5\cdot CH:C_6H_2Br_2:O.$$

2. By removing the elements of hydrogen bromide from the ψ-bromides formed by the action of bromine on phenols.

$${}^{H}_{CH_2Br}\!>C_6Br_4:O(\text{or } CH_2Br\cdot C_6Br_4\cdot OH)\text{—}HBr$$
$$= CH_2:C_6Br_4:O.$$

The reaction is effected by shaking a benzene solution of the ψ-bromide with anhydrous sodium acetate. The tetrabromoquinomethane taken as an example is an amorphous white powder which easily adds hydrogen bromide, water, &c. (Zincke and Böttcher, Annalen, 1905, 343, 100).

3. By dehydration of *p*-hydroxyaryl carbinols

$$(C_6H_5)_2C(OH)(C_6H_4OH)$$
$$= H_2O + (C_6H_5)_2C : C_6H_4 : O,$$

V. Baeyer and Villiger obtained diphenylquinomethane by heating *p*-hydroxytriphenylcarbinol. At 90° only half a molecule of water is eliminated, but a new evolution of water vapour takes place at 150°. The resulting vitreous mass was crystallised from a mixture of ether and benzene ; orange needles, m.p. 168° (Ber. 1903, 36, 2792).

4. By heating *p*-methoxytriarylmethyl halides. Bistrzycki and Herbst (Ber. 1903, 36,

2335) obtained diphenylquinomethane by heating anisyldiphenylmethyl chloride for 1 hour at 180°–200°.

$$(C_6H_5)_2CCl(C_6H_4OCH_3) \\ =CH_3Cl+(C_6H_5)_2C:C_6H_4:O$$

Staudinger (Ber. 1908, 41, 1355; *see* also Staudinger and Bereza, Annalen, 1911, 380, 243) finds that ketenes react in the cold with quinones giving β-lactones. The latter, when carefully heated below their melting-point, give quinomethanes.

$$(C_6H_5)_2C{:}C{:}O+O{:}C_5H_4{:}O \\ =(C_6H_5)_2C\overline{\angle CO.O\lrcorner}C_6H_4{:}O \\ =CO_2+(C_6H_5)_2C{:}C_6H_4{:}O.$$

The corresponding imines are known in some cases. Baeyer, Villiger and Hallensleben (Ber. 1903, 36, 2794) allowed phenylmagnesium bromide to react with p-amino-benzophenone, isolated the aminotriphenylcarbinol as picrate, liberated the colourless carbinol base and heated to 160° in a current of hydrogen. The analytical figures obtained for an anhydro-compound, $C_{19}H_{15}N$, are not quite satisfactory. The substance subsequently proved to be a dimeric form (Ber. 1904, 37, 604).

Baeyer and Villiger obtained sharp analytical figures and good results for simple molecular weight with the phenylimine of diphenylquinomethane, $(C_6H_5)_2C{:}C_6H_4{:}N{\cdot}C_6H_5$, m.p. 133°–138°. This red crystalline substance is liberated directly from its salts by the action of alkalis. Treatment with dilute acids gives the corresponding colourless carbinol, whilst stronger acids give the coloured salts of the phenylimine (Baeyer and Villiger, Ber. 1904, 37, 608).

The quinomethanes and their imines are chiefly noted for the ease with which a molecule of water, acid, &c., is added. Thus tetrabromoquinomethane regenerates the ψ-bromide with hydrobromic acid, alkalis in acetone solutions give tetrabromohydroxybenzyl alcohol and tetrabromohydroxybenzyl-acetone.

$$CH_2{:}C_6Br_4{:}O+H_2O=HO{\cdot}CH_2{\cdot}C_6Br_4{\cdot}OH$$
$$CH_2{:}C_6Br_4{:}O+CH_3{\cdot}CO{\cdot}CH_3 \\ =CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6Br_4{\cdot}OH.$$

Diphenylquinomethane (fuchsone) is reduced by zinc and acetic acid to hydroxytriphenylmethane, and on boiling with dilute potash adds the elements of water, giving hydroxytriphenyl carbinol. On the other hand, p-trihydroxytriphenyl carbinol is incapable of existence, losing water and passing into dihydroxyfuchsone or pararosolic acid.

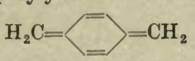
Whilst the carbinol bases are colourless, the quinonoid anhydro-bases are coloured, although their shade differs considerably from that of their salts. The following table, due to Willstätter, shows this clearly.

Imine.	Colour of Solution.	Salts.	Reference.
$C(C_6H_5)_2{:}C_6H_4{:}N\text{-}C_6H_5$	Red		B. & V., Ber. 1904, 37, 597
$C(C_6H_5)(C_6H_4{\cdot}NH_2){:}C_6H_4{:}NH$	Yellow	Döbner's violet	B. & V., Ber. 1904, 37, 2848
$C(C_6H_5)(C_6H_4{\cdot}NHC_6H_5){:}C_6H_4{:}N{\cdot}C_6H_5$	Brownish-red	Viridine	B. & V., Ber. 1904, 37, 2848
$C(C_7H_6{\cdot}NH_2)_2{:}C_7H_6{:}NH$	Orange-yellow	New fuchsine	W. & P., Ber. 1908, 41, 1458
$C(C_6H_4{\cdot}NHC_6H_5)_2{:}C_6H_4{:}N{\cdot}C_6H_5$	Red-brown	Aniline blue	B.&V., Ber. 1904, 37, 2848
$C[C_6H_4{\cdot}N(CH_3)_2]_2{:}C_1H_6{:}NC_2H_5$	Orange-yellow	Victoria blue R.	N. & P., Ber. 1908,41, 579

In the above, B. and V. stands for Baeyer and Villiger, W. and P. for Willstätter and Piccard, and N. and P. for Nölting and Philipp. Besides the references given, the following papers may also be consulted: Auwers, Ber. 1911, 44, 788; Bistrzycki, *ibid.* 1901, 34, 3073; 1903, 36, 3558, 3565; 1912, 45, 1429; Baeyer and Villiger, *ibid.* 1904, 37, 1183, 3191; Annalen, 1907, 354, 152; Zincke, J. pr. Chem. 1898, ii. 58, 441; 59, 228; Annalen, 1903, 329, 1; 1908, 363, 246.

QUINODIMETHANES.

The simplest quinonoid hydrocarbon, quinodimethane or p-xylylene



has not been isolated; several derivatives have, however, been prepared. Removal of bromine from diphenyl-p-xylylene dibromide,

$$C_6H_5{\cdot}CHBr{\cdot}C_6H_4{\cdot}CHBr{\cdot}C_6H_5,$$

by means of mercury or silver gives a yellow substance which is probably diphenyl-p-xylylene; it is, however, too unstable to isolate (Thiele and Balhorn, Ber. 1904, 37, 1465). Sufficient stability is usually secured by replacing the four hydrogen atoms of the methylene groups by hydrocarbon radicles.

METHODS OF PREPARATION.

(i.) By removing bromine from substituted p-xylylene dibromides. The dimethyl ether of tetraphenyl-p-xylylene glycol,

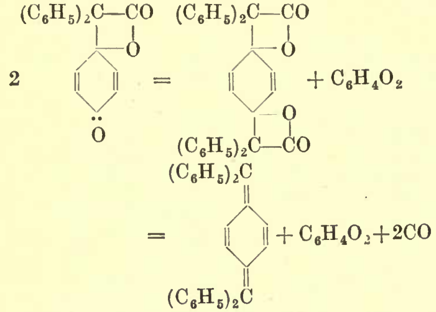
$$(C_6H_5)_2C(OCH_3){\cdot}C_6H_4{\cdot}C(OCH_3)(C_6H_5)_2,$$

is obtained from dimethyl terephthalate by the Grignard reaction and converted into the corresponding dibromide by a solution of hydrogen bromide in glacial acetic acid. The tetraphenyl-p-xylylene dibromide is dissolved in 50 times its weight of benzene and boiled in the dark for 20 hours with 1½ times its weight of molecular silver.

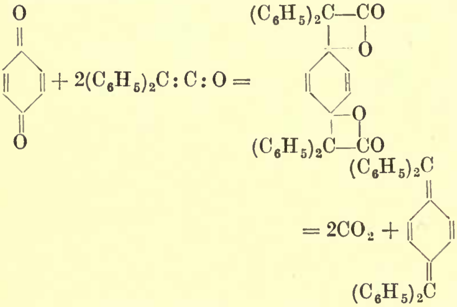
$$(C_6H_5)_2CBr{\cdot}C_6H_4{\cdot}CBr(C_6H_5)_2+2Ag \\ =2AgBr+(C_6H_5)_2C{:}C_6H_4{:}C(C_6H_5)_2.$$

The solution is filtered hot and frozen. On allowing the benzene to melt, a residue of the quinonoid hydrocarbon is left; less pure material is contained in the mother-liquor. The substance is crystallised in absence of light and air from petroleum of b.p. 100°–130° (Thiele and Balhorn, Ber. 1904, 37, 1469).

(ii.) Tetraphenylquinodimethane is formed when the mono-β-lactone obtained from diphenylketene and quinone is heated in a high boiling-point solvent.



(iii.) A better way is to add an excess of diphenylketene to a solution of quinone in petroleum ether. On standing for a day, the di-β-lactone decomposes spontaneously (Staudinger, Ber. 1908, 41, 1355).

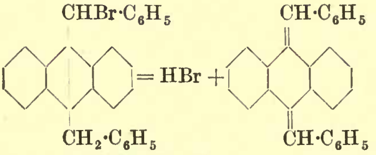


A modified method consists in fusing diphenylketenequinoline with the necessary quinone in an atmosphere of carbon dioxide (Staudinger and Bereza, Annalen, 1911, 380, 243).

(iv.) Hydrogen chloride may be removed from compounds of the type of *p*-benzhydryltriphenylchloromethane on boiling with xylene and quinoline (Tschitschibabin, Ber. 1908, 41, 2770).

$$(C_6H_5)_2CCl{\cdot}C_6H_4{\cdot}CH(C_6H_5)_2+C_9H_7N$$
$$=C_9H_7N{\cdot}HCl+(C_6H_5)_2C{:}C_6H_4{:}C(C_6H_5)_2.$$

Dibenzaldihydroanthracene is obtained by eliminating hydrogen bromide from bromodibenzylanthracene (Lippmann and Fritsch, Monatsh, 1904, 25, 793).



Tetraphenylquinodimethane forms shining needles of the colour of powdered potassium dichromate; m.p. 239°–242° (Thiele and Balhorn), 240° (Tschitschibabin), 240°–242° (Staudinger). Difficultly soluble in all solvents; the solutions are intensely yellow or orange in colour and show strong gold coloured fluorescence. The colour of the solutions fades quickly on exposure to light. Bromine is added immediately and iodine liberated from hydrogen iodide in carbon tetrachloride solution. Baeyer supposes the colour of the compound may be explained by the existence of double carbonium linkages (Ber. 1905, 38, 576).

The following similar quinonoid compounds have been obtained.

***p*-Bromotetraphenylquinodimethane,** m.p. 257°–259°. Tschitschibabin.

Triphenyl-*p*-tolylquinodimethane, m.p. 197°, Tschitschibabin.

Triphenyl-α-naphthylquinodimethane, m.p. 240°–241°, Tschitschibabin.

Tetraphenyltoluquinodimethane, m.p. 200°–210°, Staudinger and Bereza.

Tetraphenylchlorotoluquinodimethane, m.p. 195°–200°, Staudinger and Bereza.

Tetraphenyl-*m*-dichlorotoluquinodimethane, m.p. 225°, Staudinger and Bereza.

Tetraphenyl-*p*-xyloquino-2 : 5-dimethane, m.p. 200°, Staudinger.

Tetraphenyl-α-naphthoquinodimethane, m.p. 262°–263°, Staudinger.

Diphenylanthraquinodimethane, m.p. 234°–236°, Lippmann and Fritsch.

Tetraphenyldiphenoquinodimethane

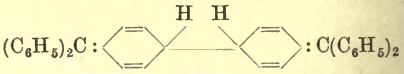
$$(C_6H_5)_2C : C_6H_4 : C_6H_4 : C(C_6H_5)_2.$$

By the action of metals (zinc, silver, copper, &c.) on solutions of the dichloro-compound

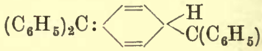
$$(C_6H_5)_2CCl{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CCl(C_6H_5)_2.$$

The solution acquires the colour of permanganate. On evaporation of the solvent, the hydrocarbon is left as a violet powder which, in a moist condition, absorbs oxygen rapidly (Tschitschibabin, Ber. 1907, 40, 1818).

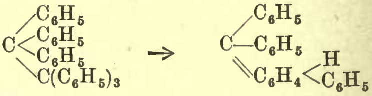
Pyrene, as will be seen from its structure (*v. s.*), must be classed as a quinonoïd hydrocarbon; and quinonoïd formulæ have been suggested for the so-called 'triphenylmethyl' obtained by Gomberg by the action of metals on triphenylmethyl chloride. Heintschel (Ber. 1903, 36, 320, 579) has suggested the structure



whilst Jacobson (*ibid.* 1905, 38, 196) thinks most of the reactions of the substance agree with the formula



Gomberg supposes that the structures



are tautomeric (Ber. 1907, 40, 1881).

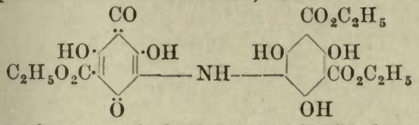
Amongst many papers dealing with the structure of 'triphenylmethyl,' the following may be consulted: Tschitschibabin (Ber. 1907, 40, 1810, 3056); Schlenk, Mair and Bornhardt (*ibid.* 1911, 44, 1169); Wieland (Annalen, 1911, 381, 200; Ber. 1911, 44, 2250, 2557). Wieland's discovery that the peroxide of triphenylmethyl gives tetraphenyldiphenoxyethane,

$$(C_6H_5)_2(C_6H_5O)C{\cdot}C(OC_6H_5)(C_6H_5)_2,$$

seems to be important.

The attempts of Staudinger and Clar (Ber. 1911, 44, 1623) to prepare quinoketenes of the types, $O : C : C_6H_4 : C{:}O$, $(C_6H_5)_2C{:}C_6H_4{:}C{:}O$, and $O{:}C{:}C_6H_4{:}C{:}C_6H_4{:}C{:}O$, proved unsuccessful:

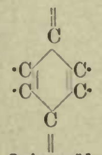
a substance is, however, known to which a quinomonoketene structure, viz. :—

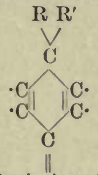


has been ascribed (Leuchs and Theodorescu, Ber. 1910, 43, 1239).

HEMIQUINOÏD COMPOUNDS.

Several compounds already referred to contain a grouping which can be described as hemiquinonoïd. The *cyclo*-hexadiene ring is intact but the carbonyl group (or its equivalent $>C:N-$, $>C:C<$) is only found once, the other carbonyl group being represented by a carbon atom attached to two monovalent radicals

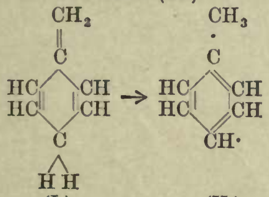

Quinonoïd.



Hemiquinonoïd.

HYDROCARBONS.

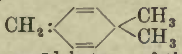
Instead of the term 'hemiquinonoïd,' Auwers refers to compounds of this type as 'semi-benzenoïd.' The parent substance of the group would be a hydrocarbon of structure (I). It is probably incapable of existence, and any reactions devised for obtaining it would result in the production of toluene (II.).



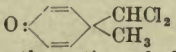
(I.) (II.)

A dimethyl derivative shows sufficient stability for isolation (Auwers and K. Müller, Ber. 1911, 44, 1595).

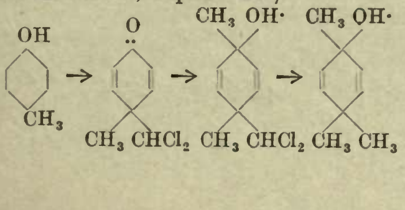
1 : 1-Dimethyl-4-methylene *cyclo-* $\Delta^{2,5}$**-hexadiene** C_9H_{12} or



A hemiquinonoïd ketone of the structure



is prepared by the action of chloroform and sodium hydroxide on *p*-cresol (Ber. 1905, 38, 1705). This reacts normally with magnesium methyliodide, yielding a carbinol which need not be isolated before reduction in moist ether-alcohol solution to trimethyl-*cyclo*-hexadiene-ol (colourless needles, m.p. 43°–44°).

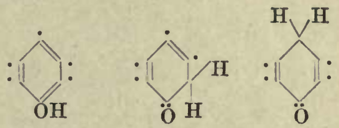


The carbinol loses a molecule of water when shaken for 20 minutes with 10 p.c. sulphuric acid and ice. The resulting 1 : 1-dimethyl-4-methylene-*cyclo*-$\Delta^{2,5}$-hexadiene is extracted with ether, the ethereal extract dried over calcium chloride and distilled under reduced pressure : b.p. 50° at 23 mm. ; unstable. The molecular refraction and dispersion are far higher than for the isomeric benzenoïd compounds (mesitylene, pseudo-cumene and methylethylbenzene).

Other papers by Auwers on compounds of 'semibenzene' type may be referred to (Ber. 1903, 36, 1861, 3902 ; 1905, 38, 1697 ; 1906, 39, 3748 ; Annalen, 1907, 352, 219, 273, 288 ; Ber. 1910, 43, 3094 ; 1911, 44, 588, 788, 1595, 3679).

PSEUDOPHENOLS.

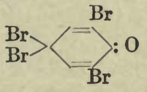
If the idea of keto-enolic tautomerism is extended to the phenols, each hydroxy-derivative of benzene corresponds to two keto*cyclo*-hexadienes



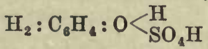
In the case of phenol and its simpler derivatives, the possibility of isolating desmotropic forms appears to be remote, the tribromophenol bromide $C_6H_2OBr_4$, obtained by adding strong bromine water to a solution of phenol in 600–1000 parts of water, and to which Benedikt (Annalen, 1879, 199, 128 ; Monatsh. 1880, 1, 360) assigned the constitution

$$2:4:6\text{-}C_6H_2Br_3.OBr\ ;$$

is almost certainly to be formulated as

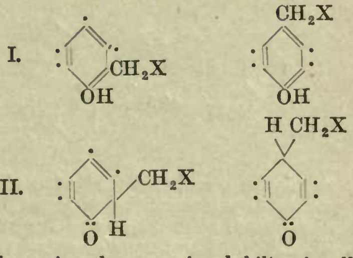


(Thiele and Eichwede, Ber. 1900, 33, 673), for on digestion with lead acetate in acetic acid, 2 : 6-dibromoquinone is produced. It has been suggested that mineral acids and phenols yield oxonium salts derived from the ketonic form (Chem. Soc. Trans. 1904, 85, 1229) ; *e.g.*



$$H_2:C_6H_4:O\begin{matrix}\diagup H\\ \diagdown SO_4H\end{matrix}$$

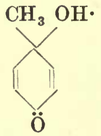
The homologues of phenol when treated with an excess of halogen, yield products insoluble in alkali (Auwers, Ber. 1895, 28, 2888, 2902, 2910 ; Zincke, *ibid.* 3121). To the 'pseudophenols,' the structure of true phenols (I) or of the desmotropic ketones (II)



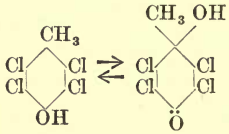
may be assigned : mere insolubility in alkali is not a sufficient argument to decide in favour of the ketonic structure.

PSEUDOQUINOLS.

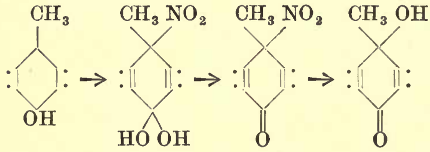
In the case of the pseudoquinols ('chinole,' Bamberger), the hemiquinonoïd structure is necessary, the lowest member of these homologues of quinol has the constitution



The first monocyclic ψ-quinol was obtained by Zincke (Ber. 1895, 28, 3121), tetrachloro-*p*-cresol when treated with nitric acid adds an atom of oxygen; the ψ-quinol thus produced regenerates tetrachloro-*p*-cresol on reduction.

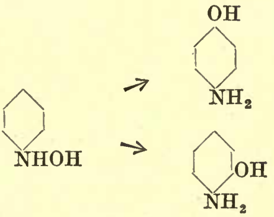


The conversion of the *p*-substituted phenol to pseudoquinol may be explained by (i.) addition of the elements of nitric acid, (ii.) elimination of water with production of a nitroketone (quinitrol), (iii.) hydrolysis of the quinitrol

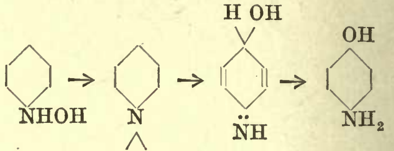


In many cases quinitrols have been isolated.

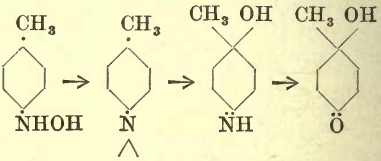
The discovery of the halogen-free pseudoquinols resulted from experiments (Bamberger, Ber. 1900, 33, 3600) made in order to explain the mechanism of the reaction in which β-phenylhydroxylamine is isomerised by sulphuric acid to *p*-aminophenol (Bamberger, *ibid.* 1894, 27, 1349, 1552; Wohl, *ibid.* 1434). Similar reactions were observed in cases where the *p*-position to the hydroxylamino-group was unoccupied; with a *p*-halogen atom derivatives of *o*-aminophenol were obtained, and even in the case of hydroxylaminobenzene itself, *o*-aminophenol is produced by the action of alcoholic sulphuric acid



It should be mentioned that with alcoholic sulphuric acid, *p*-phenetidine is formed under certain conditions (Bamberger and Lagutt, Ber. 1898, 31, 1500). Bamberger assumed that in the ordinary reaction the first action of sulphuric acid was to remove the elements of water with production of an 'aryl-imide,' Ar·N<, that this adds water giving an 'imidodienol' which then rearranges itself to a *p*-aminophenol

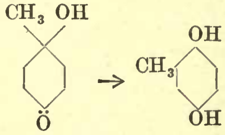


If such a β-arylhydroxylamine be alkyl substituted in the para position to the hydroxylamino-group the last stage is evidently impossible, but the imino group will be hydrolysed by the acid and a pseudoquinol result

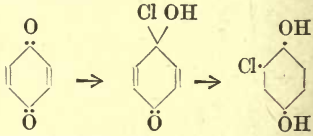


(Bamberger, Ber. 1900, 33, 3600; 1901, 34, 61; 1912, 390, 131; Zincke, *ibid.* 253).

The continued action of dilute sulphuric acid on the pseudo-quinol causes isomerisation



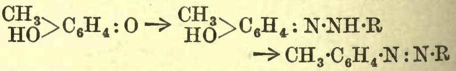
The reaction takes place very slowly in the cold, more rapidly on warming. Possibly the action of the hydracids on quinone is to be explained in a similar manner.



Pseudoquinols are also obtained by the action of Grignard's reagents on quinones (Bamberger and Blangey, Ber. 1903, 36, 1625).

REACTIONS.

(i.) The hydrazones of the ψ-quinols lose water and give azo- compounds.

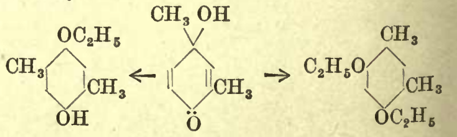


$$\substack{CH_3\\HO}\!>\!C_6H_4:O \rightarrow \substack{CH_3\\HO}\!>\!C_6H_4:N{\cdot}NH{\cdot}R \rightarrow CH_3{\cdot}C_6H_4{\cdot}N:N{\cdot}R$$

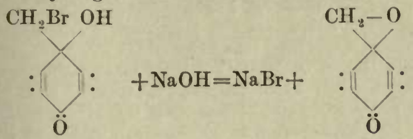
(Bamberger, *ibid.* 1902, 35, 1424).

(ii.) By reduction, phenols are obtained.

(iii.) With alcoholic sulphuric acid, derivatives of quinol and resorcinol are obtained, *e.g.* xylo-ψ-quinol gives a mixture of the monoethyl ether of *p*-xyloquinol and the diethyl ether of *m*-xylorcin.



(iv.) Pseudoquinols with the group CH_2Br lose hydrogen halide on treatment with soda



Methyl-ψ-quinol $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6H_4:O$. The product of the transformation of this compound, homoquinol $C_6H_3(CH_3)(OH)_2$ was obtained by the action of dilute sulphuric acid on *p*-hydroxylaminotoluene (Bamberger, Festschrift Zurich, 1896, ii. 179). The ψ-quinol was subsequently isolated, its reactions with hydrazines are described by Bamberger at a later date (Ber. 1902, 35. 1426); m.p. 75°–76° (Annalen, 1912, 390, 165).

Tetrachloro-methyl-ψ-quinol $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6Cl_4:O$, by oxidation of tetrachloro-*p*-cresol with warm nitric acid. Gives an *acetyl derivative* (Zincke, Ber. 1895, 28, 3122). Cold nitric acid yields a *nitro ketone* $\begin{smallmatrix}CH_3\\NO_2\end{smallmatrix}>C_6Cl_4:O$ (Zincke, *ibid.* 1901, 34, 258).

Tribromo methyl-ψ-quinol $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6HBr_3:O$, m.p. 128°, *acetyl derivative*, m.p. 127°–128°.

Tetrabromo-methyl-ψ-quinol $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6Br_4:O$, m.p. 205°; *acetyl derivative*, m.p. 175°–176; *nitro-ketone* $\begin{smallmatrix}CH_3\\NO_2\end{smallmatrix}>C_6Br_4:O$ (Zincke, Ber, 1901, 34, 258).

2 : 4-Dimethyl-ψ-quinol $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6H_3(CH_3):O$. By the action of a mixture of 1 part concentrated sulphuric acid and 20 parts of water on 2 parts of *m*-xylylhydroxylamine

$$(NHOH : CH_3 : CH_3=1 : 2\quad 4).$$

The mixing is effected at 15°, the reaction continues 8–10 days at 22°–25° in vessels filled with carbon dioxide. Filter from precipitate, extract the latter with boiling water, add washings to filtrate, acidify the liquid with a mixture of 4 grms. sulphuric acid and 4 grms. of water and extract 50–60 times with ether. Dry the ethereal extract with calcium chloride, distil off the solvent, remove any adhering oil from the residue and recrystallise from a small quantity of boiling water, decolourising with animal charcoal. The ψ-quinol separates as a colourless hydrate, $C_6H_{10}O_{21},H_2O$, yield 60 p.c. of the theoretical. Colourless rhombic prisms, m.p. 73°–73·5°. Difficultly soluble in cold, easily in boiling water, readily soluble in organic solvents, petroleum ether excepted. Exhibits weak acid character; the sodium hydroxide solution assumes in succession yellow, brown, and violet-red shades if air be allowed access. In absence of air, alkalis effect isomerisation to *p*-xyloquinol ($CH_3 : CH_3 : OH : OH=1:4:2:5$), ferric chloride soon produces the smell of xyloquinone. *Benzoyl derivative*

$$\begin{smallmatrix}CH_3\\C_6H_5CO\cdot O\end{smallmatrix}>C_6H_3(CH_3):O,$$

m.p. 72·5°–73·5° (Bamberger and Brady, Ber. 1900, 33, 3642).

Tribromo-derivative $\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6Br_3(CH_3):O$, from *tribromo-m*-xylenol and nitric acid, m.p. 176° (Zincke, Ber. 1901, 34, 258).

Tribromo-ethyl-ψ-quinol $\begin{smallmatrix}C_2H_5\\HO\end{smallmatrix}>C_6HBr_3:O$, m.p. 105°.

Tetrabromo-ethyl-ψ-quinol $\begin{smallmatrix}C_2H_5\\HO\end{smallmatrix}>C_6Br_4:O$ (Zincke, *l.c.*).

2 : 4 : 6-Trimethyl-ψ-quinol

$$\begin{smallmatrix}CH_3\\HO\end{smallmatrix}>C_6H_2(CH_3)_2:O.$$

From mesitylhydroxylamine, m.p. 45·5°–46°. *Benzoyl derivative*, m.p. 128·5° (Bamberger and Rising, Ber. 1900, 33, 3636).

Hemiquinonoïd formulæ have been assigned to several classes of compounds. Heintschel's and Jacobson's formulæ for 'triphenylmethyl' are of this type as are also the formulæ proposed by Cain and Morgan for the aromatic diazonium salts.

Papers relating to ψ-quinols, ψ-bromides and quinitrols.

Auwers and co-workers: 1895, Ber. 28, 2888, 2902, 2910; 1896, *ibid.* 29, 1095, 1110, 1120, 1129, 2329, 2348; 1897, *ibid.* 30, 744, 753, 755; 1898, Annalen, 301, 203, 266; 302, 76, 99, 107, 131; Ber. 1899, 32, 2978, 3005, 3016, 3034, 3273, 3281, 3297, 3309, 3317, 3440, 3454, 3466, 3475, 3583, 3587, 3598; 1901, *ibid.* 34, 4256, 4267; 1902, *ibid.* 35, 114, 124, 131, 144, 425, 443, 455, 465, 4207; 1903, *ibid.* 36, 1861, 1878; 1904, Annalen, 334, 264; 1905, Ber. 38, 1693, 3302; 1906, Annalen, 344, 93, 141, 171, 194, 227, 257.

Bamberger and co-workers: 1900, Ber. 33, 3600, 3623, 3636, 3642; 1902, *ibid.* 35, 1424, 3886; 1903, *ibid.* 36, 2028; 1907, *ibid.* 40, 1893, 1906, 1908, 1918, 1932, 1949, 1956.

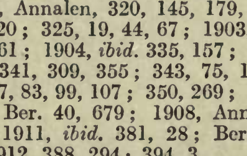
Fries and co-workers: 1906, Ber. 39, 435; 1907, Annalen, 353, 325; 1908, Ber. 41, 2614; 1909, *ibid.* 42, 3375, 3381.

Stephani: Ber. 1901, 34, 4283.

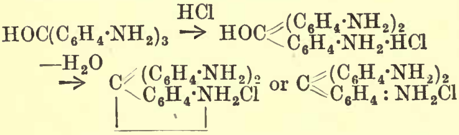
Zincke and co-workers: 1895, Ber. 28, 3121; 1897, J. pr. Chem. ii. 56, 157; 1898, *ibid.* ii. 58, 441; 1900, *ibid.* ii. 61, 561; 1901, *ibid.* ii. 63, 183; 1902, Annalen, 320, 145, 179, 199, 220; 322, 174, 220; 325, 19, 44, 67; 1903, *ibid.* 328, 261; 330, 61; 1904, *ibid.* 335, 157; 1905, *ibid.* 338, 236; 341, 309, 355; 343, 75, 100; 1906, *ibid.* 349, 67, 83, 99, 107; 350, 269; 1907, *ibid.* 353, 357; Ber. 40, 679; 1908, Annalen, 362, 201, 221; 1911, *ibid.* 381, 28; Ber. 44, 176; Annalen, 1912, 388, 294; 394, 3.

QUINONOÏD REARRANGEMENT.

Under this heading, the linkage changes represented schematically by



will be considered. The rearrangement from benzenoïd to quinonoïd configuration will receive most attention as it is reversible. Reference has already been made to the assumption that coloured organic compounds possess a quinonoïd structure (*v.s.* this article and CHROMOPHORES), the first steps in this direction being undoubtedly due to the researches of Otto and Emil Fischer on the dyestuffs of the rosaniline group (Annalen, 1878, 194, 272). Coloured pararosaniline (salt) yields a colourless base on treatment with alkali (A. Rosenstiehl, Ann. Chim. Phys. 1876, v. 8, 192), the compound obtained by the action of potassium cyanide is also colourless (H. Müller, Zeitsch. f. Chem. 1866, 2; O. and E. Fischer, Annalen, 1878, 194, 274), and so is the paraleukaniline (as well as its salts with acids) obtained by reduction (Hofmann, Jahresb. 1862, 349; O. and E. Fischer, Annalen, 1878, 194, 268). Paraleukaniline is undoubtedly triaminotriphenylmethane, as proved both by its conversion into and derivation from triphenylmethane; the cyano-derivative is triaminotriphenylacetonitrile, and the colourless pararosaniline base may be assumed to have the corresponding structure of a carbinol (*cf.* Hantzsch and Osswald, Ber. 1900, 33, 278). In the case of salt formation, the base does not simply add one or more equivalents of acid, but water is eliminated at the same time; a property usually found associated with ammonium bases with which the pararosaniline base has nothing in common, since it is practically insoluble in water, soluble in organic solvents, and has not the strong alkaline reaction of an ammonium hydroxide. In many cases the colourless carbinol bases of the triphenylmethane group dissolve in cold dilute acids with very little colouration. This, however, develops on standing or warming. The relations between base and salt can be explained by the following scheme.



$$\mathrm{HOC(C_6H_4{\cdot}NH_2)_3} \xrightarrow{\mathrm{HCl}} \mathrm{HOC}{<}\begin{matrix}\mathrm{(C_6H_4{\cdot}NH_2)_2}\\ \mathrm{C_6H_4{\cdot}NH_2{\cdot}HCl}\end{matrix} \xrightarrow{-\mathrm{H_2O}} \mathrm{C}{<}\begin{matrix}\mathrm{(C_6H_4{\cdot}NH_2)_2}\\ \mathrm{C_6H_4{\cdot}NH_2Cl}\end{matrix} \text{ or } \mathrm{C}{<}\begin{matrix}\mathrm{(C_6H_4{\cdot}NH_2)_2}\\ \mathrm{C_6H_4 : NH_2Cl}\end{matrix}$$

Both alternative formulæ given to the salt are 'quinonoïd,' the first corresponding to the peroxide formula, the second to the diketone formula of quinone. Corresponding relationships hold between the rosaniline base and the salts derived from it (E. and O. Fischer, Ber. 1880, 13, 2205; Annalen, 1878, 194, 283) and the absorption spectra of base and salts was contrasted by Hartley (Chem. Soc. Trans. 1887, 51, 165).

The discovery of the oxonium salts of dimethyl pyrone by Collie and Tickle (Chem. Soc. Trans. 1899, 75, 711) led Baeyer and Villiger to a study of the basic properties of oxygen and ultimately of the salts of triphenylmethane derivatives (Ber. 1901, 34, 2679, 3612; 1902, 35, 1189, 1201, 1754, 3013; 1903, 36, 2774; 1904, 37, 597, 1183, 2848, 3191; 1905, 38, 569, 1156). Rosenstiehl had regarded pararosaniline as possessing the constitution

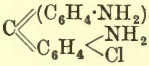
$$\mathrm{(NH_2C_6H_4)_3C{-}Cl},$$

and Baeyer proposed a carbonium structure for the triphenylmethane colouring matters. To represent the substance as a salt in which the halogen is ionisable and is not in ester combination he uses a different symbol, viz.

$$\mathrm{(NH_2C_6H_4)_3C{\sim}Cl}$$

and terms the phenomenon of the production of a coloured salt from a colourless base, *halochromy* (Ber. 1905, 38, 1156). Triphenylcarbinol itself gives coloured salts for which a quinonoïd formula was proposed (Norris and Sanders, Amer. Chem. J. 1901, 25, 54; Kehrmann and Wentzel, Ber. 1901, 34, 3815); to this Baeyer and Villiger objected (Ber. 1902, 35, 1196). The quinonoïd formula was resuscitated by Gomberg (*ibid.* 1907, 40, 1847) but again attacked by Baeyer (*ibid.* 3083).

Another 'carbonium' structure, viz.



$$\mathrm{C}{<}\begin{matrix}\mathrm{(C_6H_4{\cdot}NH_2)_2}\\ \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{NH_2}\\ \mathrm{Cl}\end{matrix}\end{matrix}$$

which is, however, quinonoïd in type, has been suggested by F. Baker (Chem. Soc. Trans. 1907, 91, 1490).

The fact that these dyestuffs are neutral salts is, however, strongly in favour of the halogen being connected with nitrogen rather than carbon, and Baeyer's identification of Homolka's base as diaminofuchsone-imine,

$$\mathrm{C({\cdot}C_6H_4{\cdot}NH_2)_2(:C_6H_4:NH)},$$

is favourable to a quinonoid structure for the salts (Ber. 1904, 37, 2869; 1905, 38, 581; compare H. Weil, *ibid.* 1896, 29, 1541, 2677; 1900, 33, 3141, and v. Georgievics, Monatsh. 1896, 17, 7; 1900, 21, 407; Ber. 1896, 29, 2015). The transient existence of a strongly dissociated ammonium base isomeric with the nearly neutral 'pseudo-base' has been rendered probable in several cases (Hantzsch and Kalb, Ber. 1899, 32, 3109).

That some coloured substances are undoubtedly quinonoïd in structure, and that quinones are themselves coloured, has led to an attempt to represent all coloured organic substances as quinonoïd (*see* especially H. E. Armstrong, Chem. Soc. Proc. 1888, 4, 27; 1892, 8, 101, 103, 143, 189, 194; 1896, 12, 42; Chem. Soc. Trans. 1905, 87, 1272; W. N. Hartley, Chem. Soc. Proc. 1892, 8, 188; Nietzki, Organische Farbstoffe).

Thus taking some of the more important classes of coloured substances, instead of the formulæ originally assigned to them, quinonoïd formulæ may be substituted. The alternative formulæ of typical compounds are given in parallel columns in the table at top of p. 523.

Reference may be made to the articles dealing with these classes of colouring matters, and the evidence for and against quinonoïd rearrangement taking place on salt formation will alone be considered. The general question of rearrangement of linkages in the molecule on salt formation has been dealt with by Hantzsch (references given under *Nitrophenols*), Decker (many papers, *see* Ber. 1907, 40, 3818; 1908, 41, 3002; Annalen, 1909, 364, 1), Kehrmann (Ber. 1906, 39, 923); Flürscheim (Chem. Soc. Trans. 1910, 97, 84).

NITROPHENOLS.

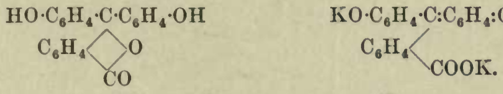
In 1892, H. E. Armstrong (Chem. Soc. Proc. 8, 102) expressed the opinion that *o*-nitrophenol, being yellow, really possesses a tautomeric formula $C_6H_4(:NO_2H)(:O)$ and suggested the name *quinoneorthonitroxime*. *p*-Nitrophenol is, however, colourless; the constitution generally

Salts of nitrophenols	$KO\cdot C_6H_4\cdot NO_2$	$O:C_6H_4:NO\cdot OK$.
Salts of nitrosophenols	$KO\cdot C_6H_4\cdot NO$	$O:C_6H_4:NOK$.
Azophenols	$C_6H_5\cdot N:N\cdot C_6H_4\cdot OH$	$C_6H_5\cdot NH\cdot N:C_6H_4:O$
Hydroxy-aldehydes and ketones	$C_6H_2\cdot CO\cdot C_6H_2(OH)_3$	$C_6H_5\cdot C(OH):C_6H_2(OH)_2:O$

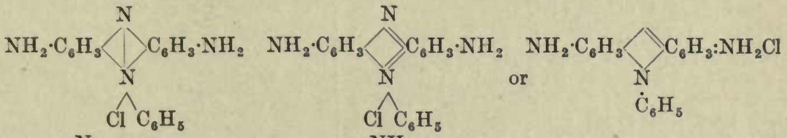
Auramine.

$(CH_3)_2N\cdot C_6H_4\cdot \underset{NH}{C}\cdot C_6H_4\cdot N(CH_3)_2HCl$ $\quad (CH_3)_2N\cdot C_6H_4\cdot \underset{NH_2}{C}:C_6H_4:N(CH_3)_2Cl$.

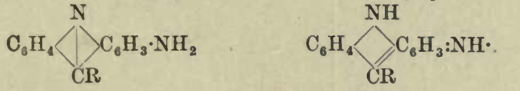
Phthaleïns.



Azines.



Acridines.



assigned to this compound was accepted, but the coloured salts were regarded as quinonoïd. The difference of volatility in a current of steam was adduced as an argument favouring a constitutional difference between the isomers; in the light of more recent work, the non-association of the molecules of the ortho- and the association of those of the para- compound (Auwers, Zeitsch. physikal. Chem. 1893, 12, 689; 1894. 15. 33; 1895, 18, 595, and other papers); Hewitt and Winmill (Chem. Soc. Trans. 1907, 91, 441; Thole, *ibid.* 1910, 97, 2596) may account for the difference in the vapour pressures of the two substances at 100°. Armstrong encountered difficulty with *m*-nitraniline; the compound can hardly be quinonoid; it is nevertheless coloured, although the benzoate is colourless.

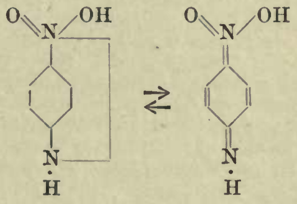
Meanwhile Hantzsch's work on pseudo-acids had appeared and afforded considerable support to the idea that acids and their salts are frequently constituted in a different manner (Ber. 1899, 32, 575, 607, 628, 641, 3066, 3089, 3101, 3137; 1901, 34, 3430; 1902, 35, 210, 226, 265, 1001, 2724; 1905, 38, 1005, 1013, 1022, 2266, 2326, 1906, 39, 139, 162, 1073, 1084, 1105, 2098, 2472, 2478, 2703, 3072, 3080, 4153; 1907, 40, 330, 1523, 1533, 1556, 4875; 1908, 41, 1745; 1909, 42, 966, 986, 1000, 1007; 1910, 43, 45, 68, 82, 95, 1685; 1911, 44, 1783). In the case of nitroform and its potassium salt, a good case was made out for the respective formulæ (Hantzsch and Rinkenberger, Ber. 1899, 32, 628) $CH(NO_2)_3$ and $C(NO_2)_2(:NO\cdot OK)$.

Hantzsch went so far as to state that any colourless hydrogen compound which gives coloured ions is a pseudo-acid; *i.e.* the free hydrogen compound and its salts possess different constitutions (Ber. 1899, 32, 578).

Other observers have explained anomalous results in the selective absorption or fluorescence of nitro-compounds by assuming the change

$$X(\cdot NO_2)(\cdot OH) \rightarrow X(:NO\cdot OK)(:O)$$

(Chem. Soc. Trans. 1900, 77, 1324; 1902, 81, 893; 1906, 89, 19), whilst Baly, Edwards and Stewart (Chem. Soc. Trans. 1906, 89, 514) concluded from a comparison of the absorption spectra of *p*-nitrophenol and its sodium salt that 'the residual affinity of the oxygen atoms of the nitro-group exerts insufficient attraction for the hydrogen of the free nitrophenol to cause the formation of the quinonoïd form, but that when the hydrogen is replaced by the more electro-positive sodium atom, then the attraction of the oxygen atom is sufficient to bring the sodium over, with the formation of the quinonoïd form.' A similar relationship was assumed in the case of orthonitrophenol and its sodium salt, whilst the yellow colour of *p*-nitroaniline was explained by its molecules existing in quinonoïd phases



The transitory existence of a meta-quinonoïd linking was also assumed to account for the phenomena observed with *m*-nitroaniline and *m*-nitrophenol. Baly and Tuck subsequently extended their views (Chem. Soc. Trans. 1906, 89, 982), stating that the phenylhydrazones of the three nitrobenzaldehydes exist partly or entirely in the quinonoïd form

$$\begin{matrix}HO\\O\end{matrix}\!>\!N:C_6H_4:C:N\cdot NH\cdot C_6H_5,$$

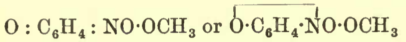
whilst *p*-nitrophenylhydrazine and its acetone derivative also exist in the quinonoïd forms

$$\begin{matrix}HO\\O\end{matrix}\!>\!N:C_6H_4:N\cdot NH_2$$

$$\text{and} \quad \begin{matrix}HO\\O\end{matrix}\!>\!N:C_6H_4:N\cdot N:C(CH_3)_2$$

Chemical evidence for the assumed change was lacking until Hantzsch and Gorke (Ber. 1906, 39, 1073) showed that under certain conditions the silver salts of the nitro-phenols yield coloured *aci*-esters on reacting with alkyl halides. These compounds are extremely labile, are readily hydrolysed and undergo spontaneous change into the nearly or quite colourless nitro-aryl-alkyl ethers. Hantzsch states that their colour points to quinonoïd structure:

certainly the ease with which they are hydrolysed is very distinct evidence in favour of the grouping: NO·O Alkyl; in this case the constitution of the methyl derivative of *o*-nitrophenol must be represented by the structure



$$O:C_6H_4:NO{\cdot}OCH_3 \text{ or } O{\cdot}C_6H_4{\cdot}NO{\cdot}OCH_3$$

As this compound is deep red and the isomeric *o*-nitroanisole practically colourless, grounds exist for assigning the structure

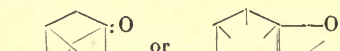
$$O:C_6H_4:NO{\cdot}OK$$

to the red potassium salt of *o*-nitrophenol. Similar observations were made with regard to the *aci*-ethyl ethers of 2:4- and 3:4-dinitrophenols and of 2:4:6-trinitrophenol. Hantzsch (Ber. 1906, 39, 1102) draws attention to the small affinity constant of 2:4:6-trichlorophenol ($2{\cdot}8\times10^{-8}$, Walker, Zeitsch. physikal. Chem. 1900, 32, 137) in comparison with trinitrophenol (0·0164, Rothmund and Druker, *ibid.* 1903, 46, 827) which points to dissimilar structures for the negative ions. Comparison of the light absorption and electric conductivity of solutions of nitrophenols points generally to a very low concentration of the second term in the equilibrium equation

$$X({\cdot}NO_2)({\cdot}OH) \rightleftharpoons X(:NO_2H)(:O) \rightleftharpoons X(:O)(:NO_2{\cdot})'+H'$$

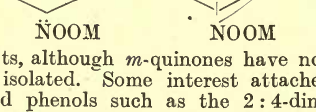
i.e. the *aci*- forms of 2:4-dinitrophenol and 2:4:6-trinitrophenol undergo practically complete dissociation; possibly in the case of *o*-nitrophenol a measurable amount of non-ionised *aci*- form exists in aqueous solution.

Hantzsch (Ber. 1906, 39, 3080) has developed similar views with regard to the hydroxy-aldehydes and hydroxy-ketones. Many cases exist in which colourless compounds of these types give coloured salts. Hantzsch assumes that the phenolic compounds give rise to quinonoïd salts, *e.g.* in the case of salicylaldehyde and its potassium salt, the following formulæ are adopted



$$C_6H_4<^{OH}_{CHO} \qquad C_6H_4\lessgtr^{O}_{CH{\cdot}OK}$$

Whilst no inherent difficulty presents itself in accepting quinonoïd formulæ for the coloured alkaline salts of *o*- and *p*-nitrophenols, the fact that *m*-nitrophenol also gives rise to coloured salts must be taken into account. Hantzsch (Ber. 1906, 39, 1095; 1907, 40, 330) assigns such formulæ as



to the salts, although *m*-quinones have not so far been isolated. Some interest attaches to substituted phenols such as the 2:4-dinitro- and 2:4:6-trinitro-derivatives. The salts and ions may be of either *o*- or *p*-quinonoid type. Hantzsch considers the *p*-type is usually preferred: comparisons of the absorption spectra of alkaline solutions of these compounds with the salts of *o*- and *p*-mononitrophenols supports this view (Buttle and Hewitt, Chem. Soc. Trans. 1909, 95, 1755). In some cases, two isomeric salts can be obtained. Rabe (Zeitsch. physikal. Chem. 1901, 38, 175) has described yellow and red thallium picrates. These observations have been further extended by Hantzsch, who suggests stereoisomerism as a possible explanation (Ber. 1907, 40, 330).

H. Kauffmann (Zusammenhang Zwischen Farbe und Constitution, Ahren's Sammlung, 1904, Enke, Stuttgart) has strongly objected to the hypothesis of a quinonoïd transformation, the alteration from practically colourless nitrobenzene to coloured metallic nitrophenolate being attributed to the auxochromic action of the metaloxyl group. Kauffmann has drawn particular attention to the yellow colour of the dimethyl ether of nitroquinol which cannot be other than $C_6H_3(OCH_3)_2NO_2$, hence a certain amount of auxochromic influence must be attributed to the methoxyl group whilst quinonoid transformation is, in this case, excluded (Ber. 1906, 39, 1959, 2722, 4237; 1907, 40, 843, 2338, 2341, 2352; 1908, 41, 4396, 4413, 4422; 1910, 43, 1214: compare Hantzsch, Ber. 1907, 40, 1556, 1572, 3536; 1908, 41, 1216).

Whilst Baly in his earlier papers (*v.s.*) attributed the difference between the absorption spectra of the nitrophenols and their salts to a radical change in constitution, he has subsequently abandoned this view (Baly, Tuck and Marsden, Chem. Soc. Trans. 1910, 97, 571). It is stated that (*l.c.* 588) 'the shape of the absorption curve of quinone and those of the nitro-compounds is quite different. It therefore seems in the highest degree improbable that the shift in the absorption bands, which takes place without any change in type when the nitrophenols are converted into their sodium salts, is due to a radical change of structure, as is demanded by the quinonoid hypothesis.'

Whether quinone and its 'nitroxime' (*i.e. aci-p*-nitrophenol) would exhibit curves of the same type is unknown. It would certainly be interesting in this connection to determine the absorption spectrum of the quinonoïd salts $C_6H_4(:NOOM)_2$ obtained by partial reduction of *o*- and *p*-dinitrobenzenes (Meisenheimer, Ber. 1903, 36, 4174; Meisenheimer and Patzig, *ibid.* 1906, 39, 2526). The constitution of such salts can hardly be other than quinonoïd.

Hantzsch's discovery of a second series of deeply coloured easily hydrolysable alkyl derivatives of the nitrophenols certainly points to a constitution of nitrophenolate ions differing from that of the nitrophenols, and it is difficult to see why an ion $NO_2X{\cdot}O'$ should be far more negative in character than $Cl{\cdot}X{\cdot}O'$ when one compares the ions, NO_2' and Cl', themselves. Moreover, the NO_2 group has different chemical properties when it is attached to radicles such as C_6H_5, $\cdot C_6H_4{\cdot}OCH_3$, &c., and when it is present in a sodium nitrophenolate. In the former case, warming with sodium methoxide solution yields an azoxy-compound with ease; in the latter case the transformation seems impossible. On the other hand, the nitrophenols in ammoniacal solution are reduced to aminophenols with great readiness in the cold. Even if the mechanism of these reduction processes is not fully understood, the different course of the reaction with compounds of the two classes (nitro-compounds and salts of nitro-phenols) points to a difference in chemical constitution.

Another case of a nitro-compound furnishing intensely coloured salts is afforded by hexanitrodiphenylamine, the ammonium salt of which was at one time employed as a dyestuff under the name of 'aurantia.' The probability of the salts having a quinonoïd structure is increased by the isolation of a violet *aci*-ether (Hantzsch and Opolski. Ber. 1908, 41, 1745); whilst further examples might be quoted in which the possibility of quinonoïd rearrangement of nitro-compounds has been suggested (*see* Meldola, Chem. Soc. Trans. 1911, 99, 1286, 2035; Dreaper, *ibid.* 2094).

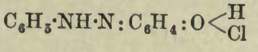
Some caution is, however, necessary, as several cases have been observed in which halogen derivatives of phenol give two series of salts, one coloured, the other colourless (Torrey and Hunter, Ber. 1907, 40, 4322; J. Amer. Chem. Soc. 1911, 33, 194; Hantzsch and Scholtze, Ber. 1907, 40, 4875. See further papers on *Chromoisomerism,* Hantzsch, *ibid.* 1910, 43, 1662, 2001, 2572; Biilmann, *ibid.* 1910, 43, 1651).

AZO-COMPOUNDS.

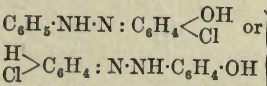
Considerable discussion has arisen with regard to the hydroxyazo- compounds, but the aminoazo- compounds have not received the same amount of attention. The *p*-hydroxyazo-compounds are undoubtedly phenolic in character; the acyl and aryl derivatives have their substituent groups attached to oxygen and not to nitrogen. Dilute nitric acid and bromine give derivatives which from the positions assumed by the nitro- groups or bromine atoms point directly to the phenolic constitution of the original azo- compounds (Hewitt and coworkers, Chem. Soc. Trans. 1900, 77, 99, 712, 810; 1901, 79, 49, 155, 160, 1090; Auwers and Mann, Ber. 1900, 33, 1312). On the other hand, Michler's hydrol behaves towards benzene azo-*a*-naphthol as it does towards quinonoïd compounds. Physico-chemical examination of the *p*-hydroxyazo- compounds also points to a phenolic formula. We may cite the association observed in hydrocarbon solvents (Auwers and Orton, Zeitsch. physikal. Chem. 1896, 21, 355; Auwers and Mann, Ber. 1900, 33, 1308), and the close similarity of the absorption spectra of the azo-phenols and their alkyl ethers (Tuck, Chem. Soc. Trans. 1907, 91, 449). The *o*-hydroxyazo-compounds generally exhibit similar behaviour. Discussion has arisen with regard to the spectroscopic evidence, Tuck considering that this favours a quinone-hydrazone structure (*l.c.* 453), whereas Auwers draws an opposite conclusion from Tuck's spectrographic measurements (Annalen, 1908, 360, 11; *cf.* Auwers, Ber. 1907, 40, 2154; Annalen, 1911, 381, 265; Charrier and Ferreri, Gazzetta, 1912, 42, ii. 811).

Whilst the metal, alkyl and aryl-derivatives of *p*-hydroxyazo- compounds are derived from the phenolic form, the salts formed with mineral acids in which the azophenols function as bases (Typke, Ber. 1877, 10, 1581; Liebermann, *ibid.* 1883, 16, 2858; Zincke and Bindewald, *ibid.* 1884, 17, 3028; Spiegel, *ibid.* 1885, 18, 1480; Lagodzinski and Matescu, *ibid.* 1894, 27, 961; dissertations of various Heidelberg students of P. Jacobson: W. Fischer, 1892; F. Marsden, 1892; J. Klein, 1892; F. Düsterbehn, 1893; C. Schwarz, 1893; B. Piepenbrink, 1895; Hewitt and Pope, Ber. 1897, 30, 1624) behave towards substituting agents as if they were derivatives of quinone-hydrazones (Hewitt and co-workers, *l.c.*; Hantzsch, Ber. 1909, 42, 2129; Fox, Chem. Soc. Trans. 1910, 97, 1337). Moreover, these salts, when hydrolysed with water, frequently yield compounds having the composition of one or two molecules of the azophenols united with one molecule of water (Hewitt, Ber. 1895, 28, 799; Hewitt and Pope, *ibid.* 1897, 30, 1624; Farmer and Hantzsch, *ibid.* 1899, 32, 3089; Hantszch and Robertson, *ibid.* 1910, 43, 106). These hydrated compounds[1] differ markedly in colour from the azophenols into which they spontaneously pass on dehydration. If the hydrates be considered as the pseudo-bases corresponding to the salts with mineral acids, their close relationship to the quinone-hydrazones is rendered evident. For the salts themselves, ammonium, oxonium, and carbonium structures have been suggested, *e.g.*

$C_6H_5{\cdot}NH(HCl){\cdot}N : C_6H_4 : O$ {Hewitt, Chem. Soc. Trans. 1900, 77, 99.



$C_6H_5{\cdot}NH{\cdot}N : C_6H_4 : O<^{H}_{Cl}$ {Fox and Hewitt, *ibid.* 1908, 93, 333; and Hantzsch, Ber. 1909, 42, 2134.



$C_6H_5{\cdot}NH{\cdot}N : C_6H_4<^{OH}_{Cl}$ or

$^{H}_{Cl}>C_6H_4 : N{\cdot}NH{\cdot}C_6H_4{\cdot}OH$ }F. Baker, Chem. Soc. Trans. 1907, 91, 1490.

The ammonium formula is negatived by the practical identity of the absorption spectra of the azophenols and their alkyl ethers in mineral acids, *i.e.* the salts are of similar type. Reasons may be given for preferring the oxonium to the carbonium formula (Fox and Hewitt, *l.c.*).

The relationships existing between benzeneazophenol and its derivatives may be exhibited by the scheme on p. 526, in which M=metal, X=Cl, SO_4H, &c., R=alkyl.

If the evidence given be accepted, it will be seen that alkalis favour a phenolic, acids a quinonoïd structure. The salts of the amino-azo-compounds, *e.g.* $C_6H_5{\cdot}N : N{\cdot}C_6H_4{\cdot}NH_2$, probably possess a quinonoïd structure

$$C_6H_5{\cdot}NH{\cdot}N : C_6H_4 : NH_2Cl$$

(Hewitt, Analyst, 1908, 33, 85; Ber. 1908, 41, 1986; Hantzsch, Ber. 1908, 41, 1171, 1187, 2435; 1909, 42, 2129; Fox, *ibid.* 1908, 41, 1989; Chem. Soc. Trans. 1910, 97, 1337).

Whilst the simpler hydroxyazo-compounds and their alkaline salts usually give solutions of yellow or brown colour, the *p*-nitro-arylazophenols, though giving brown solutions in neutral solvents, yield alkaline salts which vary from deep red (*p*-nitrobenzeneazophenol) to violet (*p*-nitrobenzeneazo-*a*-naphthol) or even pure blue. It has been suggested that this difference may be accounted for by supposing the salts to be derivatives of azo- quinones, *e.g.* $KO{\cdot}NO : C_6H_4 : N{\cdot}N : C_6H_4 : O$ (Hewitt and Mitchell, Chem. Soc. Trans. 1907, 91, 1251), though this view has been attacked by Baly, Tuck and Marsden (*ibid.* 1910, 97, 1494).

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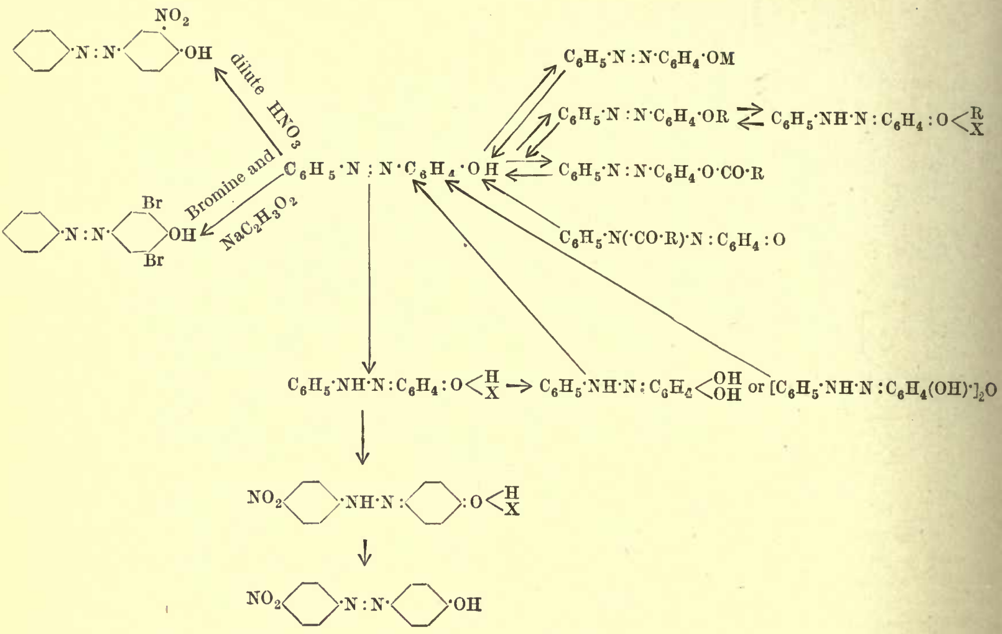
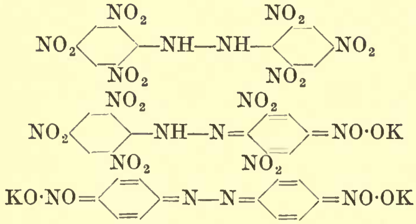
[1] The hydrates were at first mistaken for isomers (Hewitt, Ber. 1893, 26, 2975). Jacobson obtained a modification of *o*-toluene azophenol melting at about 70° (Annalen, 1895, 287, 161); this proved subsequently to be a hydrate (Ber. 1897, 30, 1628).



Whereas most azo-compounds readily undergo fission on alkaline reduction (ammonium sulphide) at the double linkage between the nitrogen atoms, such double linkage appears to be absent in the case of the alkaline *p*-nitrobenzeneazophenolates, which are easily reduced to *p*-aminobenzeneazophenol (Meldola, Chem. Soc. Trans. 1885, 47, 659).

Derivatives of hydrazobenzene nitrated in the para- position to the hydrazo- group dissolve in excess of alkali with blue colour. The pale yellow hexanitrohydrazobenzene (m.p. 201°–202°) prepared from hydrazine hydrate and picryl chloride gives both mono- and di-potassium salts; solutions of the first are deep red, of the second, deep blue to blue violet in colour (Grandmougin and Leeman, Ber. 1906, 39, 4384; 1908, 41, 1295). The relationships of the compounds may be represented by the formulæ



Compare Hewitt and Mitchell (Chem. Soc. Trans. 1907, 91, 1254); Raschig (Zeitsch. angew. Chem. 1907, 20, 2040); Hantszch and Lister (Ber. 1910, 43, 1685).

Similar formation of blue alkaline solutions in the case of 4:4′-dinitrohydrazobenzene (Lermontoff, Ber. 1872, 5, 232; Janovsky, Monatsh. 1885, 6, 160; Willgerodt, J. pr. Chem. 1890, [ii.] 42, 51; Werner and Stiasny, Ber. 1899, 32, 3272) has been frequently observed. Freundler and Beranger considered the product obtained by the reduction of di-*p*-nitroazobenzene to have a quinonoïd formula (Compt. rend. 1902, 134, 1219). Green and his co-workers bring forward evidence in favour of the substance being truly dinitrohydrazobenzene, the salts, however, being quinonoïd in structure (Chem. Soc. Trans. 1911, 99, 1960; 1912, 101, 2443).

Possibly the deep colouration given when solutions of *p*-nitrophenylhydrazones (Hyde, Ber. 1899, 32, 1810) are made alkaline may be attributed to quinonoïd transformation (compare Baly and Tuck, Chem. Soc. Trans. 1906, 89, 982). Two modifications of benzaldehyde-*p*-nitrophenylhydrazone have been observed: this also holds in the case of the *p*-nitrophenylhydrazones of the nitrobenzaldehydes (Ciusa and Vecchiotti, Atti. R. Accad. Lincei, 1911, [v.] 20, i. 803).

HYDROXYALDEHYDES AND HYDROXYKETONES.

As mentioned previously, hydroxyaldehydes and hydroxyketones in which the hydroxyl and carbonyl groups stand in the ortho- or para- position to one another, may form salts of quinonoïd type (Hantzsch, Ber. 1906, 39, 3080). The azo- derivatives of salicyl aldehydes have been examined in this respect by Hewitt and Mitchell (Chem. Soc. Trans. 1907, 91, 1262).

Schiff's bases prepared from hydroxyaldehydes occasionally occur in isomeric modifications. The isomerism is supposed by Manchot to be of phenol-quinone type (Annalen, 1912, 388, 103).

AURAMINES.

The salts of auramine bases may have a quinonoïd structure. The bases themselves cannot well have other than a ketone-imide constitution and are readily hydrolysed; the salts show greater stability. The possibility that the hydrochloride of ordinary auramine has the constitution

$$(CH_3)_2N{\cdot}C_6H_4{\cdot}C(NH_2){:}C_6H_4:N(CH_3)_2Cl$$

is supported by the existence of a methyl phenyl auramine (D. R. P. 44077) as well as by the work of A. Stock (J. pr. Chem. 1893, ii. 47, 401), which proved that the twice substituted auramines yield ketone and secondary amine on hydrolysis. Graebe (Ber. 1899, 32, 1678) has urged against this view that whilst auramine hydrochloride is easily converted into phenyl auramine by heating with aniline, it is not attacked by methylaniline. Hantzsch and Osswald (Ber. 1900, 33, 278) hold the view that the true auramine base yields a pseudo-base which loses water, giving the imine

$$\begin{aligned}&(CH_3)_2N{\cdot}C_6H_4{\cdot}C(NH_2){:}C_6H_4{:}N(CH_3)_2OH\\ &\quad\rightarrow (CH_3)_2N{\cdot}C_6H_4{\cdot}C(NH_2)(OH){\cdot}C_6H_4{\cdot}N(CH_3)_2\\ &\quad\rightarrow (CH_3)_2N{\cdot}C_6H_4{\cdot}C({:}NH){\cdot}C_6H_4{\cdot}N(CH_3)_2.\end{aligned}$$

whilst Stock (Ber. 1900, 33, 318) further supports his view by observations on phenylmethylauramine cyanide which exists in two forms, a pale yellow of benzenoïd and a yellowish-red of quinonoïd constitution.

Graebe (Ber. 1902, 35, 2615) still urges against the quinonoïd structure of the auramine salts the close resemblance which exists between them and the salts of phenyliminobenzophenone. Graebe's imino-structure has been accepted by L. Semper (Annalen, 1911, 381, 234) who finds that the pale yellow acylated auramine bases yield deep bluish-violet or bluish-green salts with acid. A quinonoïd formula is assigned to the acylated salts, *e.g.*

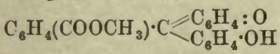
$$(CH_3)_2N{\cdot}C_6H_4{\cdot}C({\cdot}NHCOCH_3){:}C_6H_4{:}N(CH_3)_2Cl$$

but denied to the salts of auramine, methylauramine and phenylauramine on account of the great colour difference.

PHTHALEÏNS.

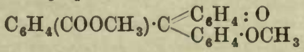
Phenolphthaleïn and its alkaline salts may well possess different structures in the sense represented by the formulæ already given; corresponding formulæ may be applied in the case of fluoresceïn and the rhodamines. The tautomerism of fluoresceïn has been demonstrated by Nietzki and Schroeter (Ber. 1895, 28, 44) who obtained a mixture of a colourless lactonoïd diethyl-ether and a yellowish-red quinonoïd ether-ester by the direct alkylation of alkali salts of fluoresceïn.

Direct evidence of this character was wanting in the case of phenolphthaleïn until comparatively recently, the supposed oxime of phenolphthaleïn prepared by Friedländer (Ber. 1893, 26, 172, 2258) not possessing the constitution originally assigned to it. The ethers obtained from phenolphthaleïn were colourless and undoubted derivatives of diphenylphthalide. A. G. Green (in part with P. E. King) has demonstrated that red quinonoïd esters



$$C_6H_4(COOCH_3){\cdot}C{<}\begin{matrix}C_6H_4{:}O\\ C_6H_4{\cdot}OH\end{matrix}$$

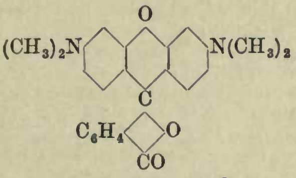
and

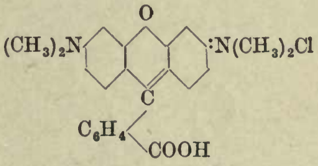


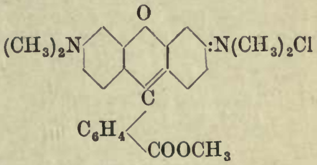
$$C_6H_4(COOCH_3){\cdot}C{<}\begin{matrix}C_6H_4{:}O\\ C_6H_4{\cdot}OCH_3\end{matrix}$$

may, however, be obtained (Ber. 1906, 39, 2365; 1907, 40, 3724; Chem. Soc. Proc. 1907, 23, 228; J. Soc. Chem. Ind. 1908, 27, 3; 1909, 28, 63). In these compounds the methyl carboxylate group is very readily hydrolysed.

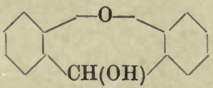
The rhodamine salts may be esterified and consequently the following formulæ probably represent the relationships existing between rhodamine base, its hydrochloride and the anisoline resulting from its esterification.

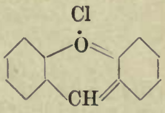






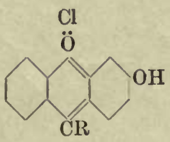
In the case of the salts with mineral acids obtained from fluoresceïn and its parent substance fluorane, an oxonium *o*-quinonoïd structure is probable. The same remark holds in the case of the simpler oxonium salts, and the relationship between xanthydrol and the salt formed from it by hydrochloric acid may be expressed in the following manner:



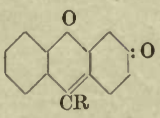


(Hewitt, Zeitsch. physikal. Chem. 1900, 34, 9; Ber. 1901, 34, 3819; Hewitt and Tervet, Chem. Soc. Trans. 1902, 81, 663; Werner, Ber. 1901, 34, 3300; Annalen, 1902, 322, 296; Fosse, Compt. rend. 1901, 133, 1218; 1902, 134, 177, and other papers).

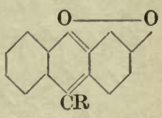
For the salts of the hydroxyxanthydrols and fluorones with mineral acids, formulæ such as



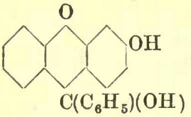
are employed. The free bases lose water, and the formulæ



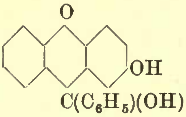
and



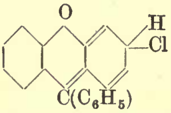
have been assigned to the anhydrides. Kehrmann favours the second formula (Ber. 1908, 41, 3440). To this Decker raises a grave objection. Of the two compounds represented by



and



the first is incapable of existence and loses water immediately, whilst the second cannot be dehydrated. If a ‘ betaine ’ oxonium phenolate formula is correct, no reason can be assigned for the fact that the second compound retains the elements of water which the first loses spontaneously (Decker, Ber. 1909, 42, 578 ; compare Pope and Howard, Chem. Soc. Trans. 1910, 97, 1023). Another view as to the constitution of the salts is that they are quinocarbonium compounds, *e.g.*



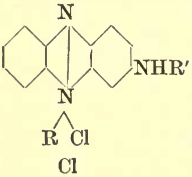
(Gomberg and Cone, Annalen, 1909, 370, 142 ; compare Hantzsch, Ber. 1910, 43, 339 ; Kehrmann, Annalen, 1910, 372, 287 ; Gomberg and Cone, *ibid.* 1910, 376, 183 ; A. Stepanoff, *ibid.* 1910, 373, 219 ; Cone and West, J. Amer. Chem. Soc. 1911, 33, 1538).

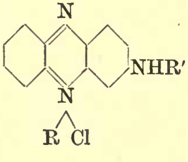
Acridine and its Derivatives.

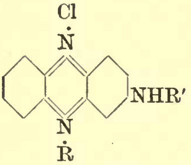
Acridine and its derivatives closely resemble the xanthene compounds except that they are more basic, the relationships between bases and salts seem to be similar (Hewitt, A. E. Dunstan and Fox, Zeitsch. physikal. Chem. 1900, 34, 13 ; Chem. Soc. Trans. 1904, 85, 529 ; 1905, 87, 1058 ; 1906, 89, 482, 1472 ; compare Flürscheim, *ibid.* 1910, 97, 94).

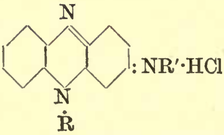
Azines.

The salts of mono-arylaminoazines will possess one of the following four formulæ

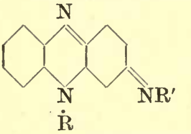


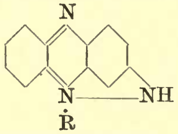




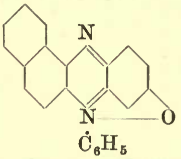


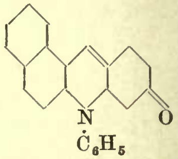
For the corresponding free bases, both of the following formulæ have been employed





Taking the first formula given for the base and one of the three first formulæ given for the salt, it would appear that there is a rearrangement from para- to ortho- quinonoïd structure on salt formation. With regard to the second formula, Kehrmann has assigned corresponding structures to the safranones, rosindones and *iso*rosindones, thus, for example, in the case of *iso*rosindone he has used a betaïne instead of a *p*-quinonoïd formula

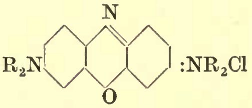




Decker and Würsch (Ber. 1906, 39, 2653) object that *iso*rosindone is not attacked by phenylmagnesium bromide, but Kehrmann (*ibid.* 1908, 41, 12) still holds the phenolbetaïne formula to be correct (compare also O. Fischer and Römer, *ibid.* 1907, 40, 3406 ; Kehrmann, *ibid.* 1908, 41, 472).

Oxazines and Thiazines.

The oxazine and thiazine dyes have been represented by the formulæ



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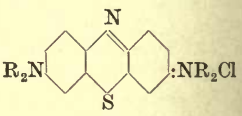
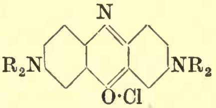
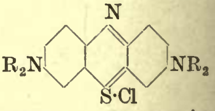


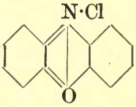
Kehrmann prefers an *o*-quinonoïd structure





representing the compounds as oxonium and sulphonium salts respectively (Ber. 1899, 32, 2601). Considerable discussion has ensued between Hantzsch (*ibid.* 1905, 38, 2146, 2577 ; 1906, 39, 153, 1365) and Kehrmann (*ibid.* 1905, 38, 2957, 4197 ; 1906, 39, 914, 1403 ; 1907, 40, 613, 1234, 1960, 2071).

Green suggested *o*-quinonoid formulæ such as



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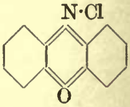
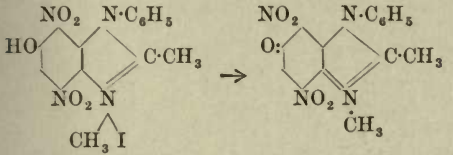


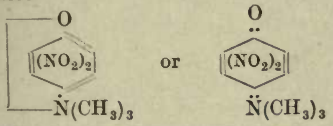
(Ber. 1899, 32, 3155) ; whilst Hewitt considered it possible that both tautomeric *o*- and *p*-quinonoïd forms exist in solution (Zeitsch. physikal. Chem. 1900, 34, 17).

Iminazolium Compounds.

A case of quinonoïd rearrangement of great theoretical interest is afforded by 4 : 7-dinitro-6-hydroxyl-1-phenyl-2 : 3-dimethylbenziminazolium iodide (Meldola and Kuntzen, Chem. Soc. Trans. 1911, 99, 1291). Boiled with water, a substance, $C_{15}H_{16}O_7N_4$ or $C_{15}H_{14}O_6N_4,H_2O$, is obtained ; the latter when completely dehydrated loses $2H_2O$. It is difficult to avoid assigning the constitution of a 4 : 7-dinitro-1-phenyl-2 : 3-dimethyl-6-benziminazolone to the dehydrated substance, the initial and final products being represented in the following manner:



The occurrence of quinquevalent nitrogen in other than ammonium combination is noteworthy and attention should also be paid to the substance

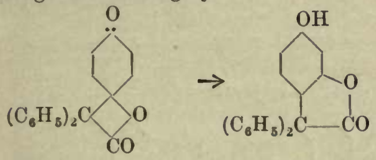


obtained by the extreme methylation of isopicramic acid (Meldola and Kuntzen, *ibid.* 2045).

Rearrangement from Quinonoïd to Aromatic Structure.

Whilst salt formation forces a quinonoïd arrangement, the benzenoïd configuration is the more stable, and many cases have been referred to above in which a substance adds on to a quinone or quinonoïd compound with production of a substituted truly aromatic compound (*e.g.* quinone and hydrogen chloride give chloroquinol).

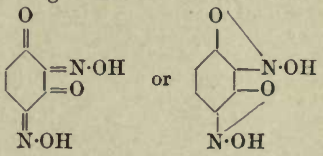
In addition to such reactions involving addition, a compound of quinonoïd (or more especially semi-quinonoïd) type undergoes intramolecular change with production of a benzenoïd compound. Examples will be found amongst the reactions of the ψ-quinols (production of monoalkyl ethers of 2 : 5-dimethylquinol and dialkyl ether of 4 : 6-dimethylresorcinol from xylo-ψ-quinol), and the production of the ψ-bromides. The transformation of the β-lactones obtained by acting with diphenyl ketone on quinone into a benzenoïd γ-lactone also belongs to this category



In all these cases we see examples of the tendency of hydroaromatic to pass into aromatic compounds. Reactions of this type are necessarily irreversible.
J. T. H.

QUINONEOXIME DYES (*Nitroso colouring matters*). The quinoneoximes can be obtained by two general methods; (1) the condensation of quinones with hydroxylamine; (2) the interaction of nitrous acid and the phenols, the latter process being the one exclusively employed in the commercial preparation of the dyes of this series. These reactions furnish oximes in which the *iso*nitroso group (NOH) is in either the para- or the ortho- position with respect to the remaining quinone oxygen; but only the ortho-compounds are of any value as colour producers. The ortho-quinoneoximes are employed as adjective dyes in conjunction with iron or chromium mordants on wool, silk, or cotton, the colour being due to the formation of an insoluble lake of the oxime and the metallic base.

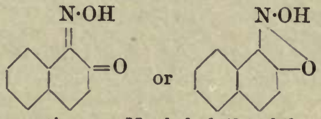
Dinitrosoresorcinol (2 · 4-*dioximinobenzo*-1 : 2 : 3 : 4-*diquinone*), which comes into commerce under the names of **resorcinol green, fast green, Alsace green, dark green in paste, chlorin, fast myrtle green,** is generally represented by one of the following formulæ:



Preparation. Resorcinol (110 kilos.) dissolved in 4500 litres of ice-cold water containing 120 kilos. of sulphuric acid is slowly treated with 144 kilos. of sodium nitrite (96 p.c.) in 400 litres of water. The product, which separates as a light yellowish-grey precipitate, is washed with water and sold as a 40–50 p.c. paste.

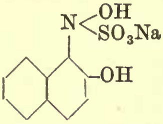
Dinitrosoresorcinol dissolves in hot water or dilute alcohol, crystallises in yellowish leaflets containing $2H_2O$, and decomposes violently at 115°; it is a moderately strong acid, decomposes carbonates and yields two series of salts. On iron mordanted wool or cotton it yields green shades very fast to soap; with chrome mordant it gives browns. Dinitrosoresorcinol was formerly used as a basis for resorcinol blue (D. R. P. 14622). When padded on cotton and steamed it furnishes a fast brown dye which serves as a mordant for basic colouring matters (Fitz, Ber. 1875, 8, 631; Goldschmidt and Strauss, *ibid.* 1887, 20, 1607; v. Kostanecki, *ibid.* 1887, 20, 3137; 1888, 21, 1405; J. Soc. Chem. Ind. 1890, 1126; Rev. gen. mat. col. 1907, 191).

1-Nitroso-β-naphthol (1 : 2-*Naphthaquinone-1-oxime*) known as **Gambine Y, Alsace green J, Mulhouse green, Naphthine S.**



Preparation. β-Naphthol (144 kilos.) is dissolved in 150 litres of hot water containing 48 kilos. of sodium hydroxide, the solution is diluted to 800 litres with ice-water, 72 kilos. of sodium nitrite (96 p.c.) are added and the solution acidified with hydrochloric or sulphuric acid. The yellow precipitate is washed with cold dilute brine solution and made into a 20–30 p.c. paste with water containing a little sodium acetate. The water used in this preparation should be free from iron, otherwise the brown shades produced with chrome mordants are considerably modified. The dilute solution may be acidified before adding the nitrite as the precipitated β-naphthol is so finely divided that it readily reacts with nitrous acid.

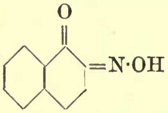
1-Nitroso-β-naphthol crystallises from alcohol or benzene in orange-brown leaflets or prisms, melting at 109°. When quite pure, it can be distilled in steam, but the commercial product generally becomes tarry on boiling with water. Wool and cotton mordanted with iron and chromium give green and brown shades respectively, the former being the faster to light. The bisulphite compound



a grey crystalline paste, produced by mixing 1-nitroso-β-naphthol with aqueous sodium bisulphite is used for printing a fast green shade on calico mordanted with iron.

The green alkali and ammonium salts of 1-nitroso-β-naphthol have also been employed in dyeing. The insoluble red cobaltic salt is used in the analytical separation of cobalt and nickel. The zinc salt is produced by digesting β-naphthol at 60°–70° with an aqueous solution of zinc sulphate and sodium nitrite; other metallic derivatives may be similarly prepared (D. R. PP. 25469, 78440; Fuchs, Ber. 1875, 8, 1026; Köhler, *ibid.* 1883, 16, 3080; Henriques and Ilinski, *ibid.* 1885, 18, 704; v. Kostanecki, *ibid.* 1887, 20, 3147; J. Soc. Chem. Ind. 1890, 1126).

2-Nitroso-α-naphthol (1 : 2-*Naphthaquinone*-2-*oxime*) sold as **Gambine R,**



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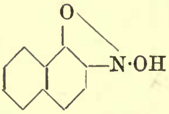
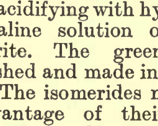


is produced together with its isomeride, 4-*nitroso-α-naphthol* (1 : 4-*naphthaquinone*-4-*oxime*) by acidifying with hydrochloric acid a cold dilute alkaline solution of α-naphthol and sodium nitrite. The greenish-yellow precipitate is washed and made into a 20–30 p.c. paste.

The isomerides may be separated by taking advantage of their differing solubilities in benzene or by precipitating their alkali salts fractionally from aqueous solution. 4-Nitroso-α-naphthol forms yellowish-white needles, decomposing at 193°–194°; 2-nitroso-α-naphthol, which predominates in the mixture, crystallises from benzene in greenish-yellow needles decomposing at 147°–148° (Ber. 1882, 15, 1816; 1884, 17, 2590; 1885, 18, 706). In practice the crude mixture of the two isomerides is employed in dyeing without removing the inert para- compound.

2-Nitroso-α-naphthol gives green and brown shades on wool mordanted with iron and chromium respectively (references, *v. supra*, 1-nitroso-β-naphthol, and Ber. 1882, 15, 1816; 1884, 17, 2065, 2589).

1-Nitroso-2 : 7-dihydroxynaphthalene (7-*hydroxy*-1 : 2-*naphthaquinone*-1-*oxime*) **Gambine H, Dioxine,**



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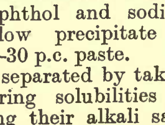


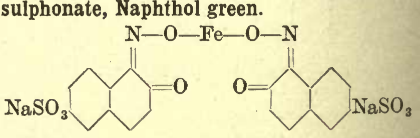
Preparation. Naphthalene (500 kilos.) and concentrated sulphuric acid (750 kilos.) are heated at 160°–170° for 6 hours, and the sulphonation carried on for 2 hours longer at 140°–150° with a further addition of 1750 kilos. of acid. The sulphonation product, poured into water, i neutralised with lime and calcium carbonate the solution of calcium naphthalenedisulphonat is filtered from calcium sulphate, treated wit sodium carbonate and crude sodium naphthalenedisulphonate obtained by evaporating th filtered solution to dryness. This sodium sal is added in portions of 150 kilos. to 300 kilos. o fused commercial sodium hydroxide containing about 10 p.c. of added water; the produc is acidified with dilute sulphuric acid, th solution boiled to expel sulphur dioxide, the cooled to 4° and treated with aqueous sodiu nitrite. The dark reddish-brown precipitate i washed, pressed, and made into 30 p.c. past with water containing a little sodium acetate.

When prepared in this way the produc contains some of the isomeric 1-nitroso-2:6 dihydroxynaphthalene. A purer preparatio is obtained by cooling the acidified solutio until 2:7-dihydroxynaphthalene crystallise out. This compound is then collected an treated in ice-cold water with the calculate amounts of sodium nitrite and dilute aceti acid. Nitroso derivatives have been prepare from the ten isomeric dihydroxynaphthalenes but only those in which the *iso*nitroso grou is in the ortho- position with respect to th quinone oxygen give coloured lakes on fabric mordanted with metallic oxides. These nitros derivatives have the general property of becoming reduced with sodium hydrosulphite t very oxidisable amino-dihydroxynaphthalene which when absorbed by textile fibres and afterwards exposed to the atmosphere, yiel intense shades of brown, grey, and black (Eng Pats. 1812, 1813, of 1890).

On wool and cotton mordanted with iro salts and dichromate respectively, 1-nitroso-2:7-dihydroxynaphthalene gives green and brown shades which are very fast to light. In conjunction with logwood extract and ferrous and copper sulphates it produces a direct black (D. R. PP. 55204, 58611; Eng. Pats. 14230, 17223, 1889; Fr. Pat. 201907; Ber. 1890, 23, 521; 1894, 27, 3050).

The foregoing gambines when condensed with tannic or gallic acid in presence of concentrated sulphuric acid give dyes producing with chrome mordant brown shades which are very fast to light and washing (D. R. P. 75633).

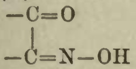
Sodium ferro-1-oximino-1 : 2-naphthaquinone-6-sulphonate, Naphthol green.

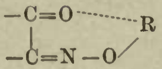


Preparation. Sodium β-naphthol-6-sulphonate (Schäffer salt) is converted by nitrous acid into sodium 1-oximino-1 : 2-naphthaquinone-6-sulphonate and 27·5 kilos. of this product, dissolved in 100 litres of water, are treated with 20 litres of ferric chloride solution (5 kilos. $FeCl_3$). The excess of iron being precipitated with sodium carbonate, the green filtrate is evaporated to dryness. The double salt may be purified either by crystallisation from alcohol or through the insoluble lead salt by decomposing the latter with sodium sulphide, carbonate or sulphate.

Wool is dyed green directly in acid baths containing iron salts, and similar shades are produced on silk in the presence of tartaric acid. The colour produced is fast to acids, alkalis, light and milling agents (D. R. PP. 28065, 28901; U. S. Pat. 316036; Eng. Pat. 2296, 1884; Fr. Pat. 160032; Ber. 1885, 18, 46; J. Soc. Chem. Ind. 1885, 4, 204; 1890, 9, 1126).

The relative stability of the coloured metallic derivatives of the ortho-quinoneoximes containing iron, chromium and cobalt, has led Werner to the view that these salts are internally co-ordinated compounds in which the metallic atom is attached to the organic chromophore (I.).


I.


II.

by both its principal and secondary valencies so as to produce a stable cyclic complex (II.) in which the metal is not readily detected by the usual qualitative tests. This hypothesis is justified by the fact that the para-quinoneoximes which could not give rise to such six-membered complexes (II.) do not behave as adjective dyes in conjunction with the metallic mordants (Werner, Ber. 1908, 41, 1062, 2383; Liebermann, *ibid.* 1436). G. T. M.

QUINOTANNIC ACID *v.* TANNINS.

QUINOVIN *v.* GLUCOSIDES.

QUINOXALINES *v.* AZINES.

QUINOXIMES *v.* AZINES.

QUISQUEITE. A lustrous, black, brittle substance, very like asphaltum in appearance, but containing much sulphur (S 46½ p.c. with C 43 p.c.) and only little hydrogen. Sp.gr. 1·75. It occurs in considerable quantity, together with patronite (*q.v.*), in a deposit of vanadium ore in the Quisque (or Minasragra) district, near Cerro de Pasco in Peru. (*See* W. F. Hillebrand, Amer. J. Sci. 1907, 24, 141; D. F. Hewett, Trans. Amer. Inst. Mining Engin. 1910, 40; 1909, 274.) L. J. S.

R

RACEMIC ACID *v.* TARTARIC ACID.

RACEMISM. The phenomenon of racemism has reference to the existence of inactive compounds or double salts of two optical enantiomorphs, which differ in certain physical and chemical properties from either active component singly or mixed in equal quantities.

Historical. Racemism was first observed by Pasteur (Leçons sur la Dissymmétrie Moléculaire, 1861; Researches on Molecular Asymmetry, Alembic Club Reprints, No. 14) in studying the crystalline forms of tartaric and racemic acids and their salts. He discovered hemihedral facets on the sodium ammonium salt of tartaric acid, and concluded that this property might be related to its rotatory power, the acid being dextrogyrate. If this were the case, then racemic acid and its salts, being optically inactive, should exhibit no such facets. To test this conclusion, he performed his well-known experiment, which consisted in crystallising sodium ammonium racemate. The result was that instead of an inactive salt without hemihedral facets, he succeeded in resolving the substance into two forms having hemihedral facets on obverse sides of the crystal, and each kind when separately dissolved and examined showed rotatory polarisation in the reverse direction.

W. Staedel (Ber. 1878, 11, 1752) who afterwards repeated the experiment only obtained the original racemate. It therefore appears that the same substance may under certain conditions crystallise as a double salt, and under others may break up into its two active components.

Scacchi (Rend. Accad. Sci. Fis. Mat. Napoli, 1865, 250) had already explained the cause of Staedel's failure by showing that the racemate separates from solution at a higher temperature than the active tartrates. Wyrouboff (Compt. rend. 1886, 102, 627) found this temperature to lie above or below 28°, and later van 't Hoff and van Deventer (Zeitsch. physikal. Chem. 1887, 1, 173) were able to show that it coincided with the transition temperature at which the tartrates lose water of crystallisation and pass into the racemate.

$$2C_4H_4O_6NaNH_4,4Aq = (C_4H_4O_6NaNH_4,2Aq)_2 + 6H_2O$$

Sodium amm. tartrate. Sodium amm. racemate.

As the change is accompanied by change in vapour pressure of the saturated solutions and in the volume of the crystals, these observers were able to fix very accurately by tensimeter and dilatometer measurements the transition temperature, which they found to be 26·7°–27·7°.

Examples of the same phenomenon have been observed in the case of other salts of tartaric acid, also of malic acid and other substances.

	Transition temp.
Sodium potassium tartrate . .	3°
Potassium tartrate . . .	37·2°
Rubidium ,, . . .	40·4°
Ammonium bimalate . . .	74°
Methyl mannoside . . .	8°
Camphoroxime	103°

Properties of racemic compounds. Racemic compounds differ in the following physical and chemical properties from their active components:—

1. *Crystalline form.* Many active substances crystallise in a different system from the racemic form: the former often exhibiting hemihedral facets, whereas the latter is usually holohedral.

2. *Specific gravity* of the two crystalline substances is different.

Substance	Specific gravity Active	Racemic
Limonene tetrabromide	2·134	2·225
Carvoxime . .	1·108	1·126
Fenchoneoxime . .	1·117	1·142
*iso*Fenchoneoxime .	1·134	1·180
Carvonetetrabromide .	2·242	2·249
Carvonetribromide .	1·958	1·958
Sobrerol	1·128	1·131

From the above table it appears that the racemic compounds have, as a rule, the greater specific gravity (Liebisch, Annalen, 1895, 286, 140; Walden, Ber. 1896, 29, 1699).

3. *Solubility and melting-point.* There appears to be a certain relation between the solubility and melting-point on the one hand, and the specific gravities on the other, of the racemic and active forms. If the specific gravity of the racemic compound is greater, the melting-point is higher and it is also less soluble. If the specific gravity is less, the melting-point and solubility are reversed. The following examples exhibit these relationships.

Substance	Sp.gr.		M.p.		Solubility	
	a.	*r.*	*a.*	*r.*	*a.*	*r.*
Malic acid .	1·595	1·601	100°	130°–131°	greater	less
Camphoric acid	1·186	1·228	187°	202°–203°	greater	less
Tartaric acid .	1·754	1·697	170°	204°	greater	less
Mandelic acid	1·341	1·300	130°	118°–119°	less	greater

4. *Absorption spectra.* These have been shown by Stewart to be different in the active and racemic forms.

5. *Water of crystallisation.* It is a common observation that the active and racemic forms usually contain different amounts of water of crystallisation.

Substance	*a.*	*r.*
Tartaric acid . . .	—	H_2O
Ammonium tartrate .	—	$2H_2O$
Potassium ,, .	$\frac{1}{2}H_2O$	$2H_2O$
Thallium ,, .	$\frac{1}{2}H_2O$	—
Sodium ,, .	$2H_2O$	$2H_2O$
Potassium lithium tartrate	H_2O	H_2O
Potassium antimonyl ,, .	$\frac{1}{2}H_2O$	$\frac{1}{2}H_2O$
Strontium glycerate .	$3H_2O$	$\frac{1}{2}H_2O$
Barium ,, . .	$2H_2O$	$\frac{1}{2}H_2O$
Calcium galactonate .	$5H_2O$	$2\frac{1}{2}H_2O$
Barium ,, . .	$5H_2O$(?)	$2\frac{1}{2}H_2O$

6. *Physiological properties.* Chabrié has shown that racemic acid is less poisonous than the active tartaric acids, and Tiemann and Schmidt noticed that inactive terpenes often have a fainter odour than the active forms.

In dilute solution the racemic compound dissociates into its two active components and consequently the solution behaves like a mixture of the two enantiomorphs. It has no action on polarised light, and such properties as vapour pressure, specific gravity, magnetic rotation and electrical conductivity (in the case of an acid) are identical with those of a mixture of the active components. The vapour density is also the same. Thus, Anschütz (Ber. 1885, 18, 1397) has shown that ethyl racemate is monomolecular when vapourised.

Methods of distinguishing racemic compounds from mixtures. The criteria for determining whether an inactive, crystalline substance is (1) a mixture or *conglomerate* of equal quantities of the two kinds of crystals not forming a compound; (2) a true *racemic compound*, that is, a compound consisting of equal molecules of the two enantiomorphs; or (3) an isomorphous mixture or mixed crystal (called also a *pseudoacemic compound*), have been examined by Bakhuis Roozeboom (Zeitsch. physikal. Chem. 1899, 28, 494) from the standpoint of the phase rule, and he has shown that the melting-point and solubility afford the most trustworthy evidence of racemism.

Melting-point of conglomerates. In this case each enantiomorph must be regarded as a separate individual and the melting-point of each (when present in excess, it may be regarded as the solvent), will be lowered by the addition of the second enantiomorph, the eutectic or mixture of minimum melting-point being reached when both are present in equal quantity. The melting-point curves of the two enantiomorphs will have the following form:—

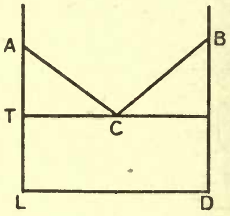


FIG. 1.

If A and B represent the melting-point of the pure lævo- and dextro- enantiomorphs (L and D), AC and CB will represent the melting-point curves of each of the enantiomorphs when mixed with increasing proportions of the other, and C the melting-point of the inactive mixture when equal quantities of the two are present. Consequently when either enantiomorph is added to the conglomerate the melting-point will be *raised.*

Melting-point of racemic compounds. The melting-point curve of a racemic compound and its two enantiomorphs will form three curves, for there are three individuals, and according to whether the racemic compound has a higher or lower melting-point than the enantiomorphs the curves will take the following forms.

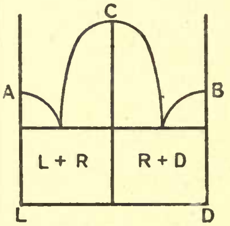


FIG. 2.

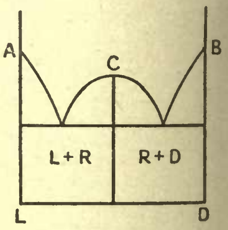


FIG. 3.

Thus active dimethyl tartrate melts at 43·3°; racemic dimethyl tartrate at 89·4°, and the curve would take form represented in Fig. 2, whilst active mandelic acid melts at 132·8° and the racemic acid at 118° and would have the form shown in Fig. 3. Here the addition of a small amount of either enantiomorph to the racemic compound will *lower* the melting-point.

Melting-point of pseudoracemic mixed crystals. If the two enantiomorphs are isomorphous and form mixed crystals they form only a single phase and the fusion-point will depend upon the composition of the solid which separates from the fused mass. If it is identical with that of the fused mass, a constant melting-point for any mixture is obtained. This has been observed in the case of the two active camphoroximes. The curve is then a horizontal line joining the melting-points of the enantiomorphs, Fig. 4.

This property is exhibited by 1-amyl-3-nitrophthalates; the compounds themselves and mixtures melt at 116°, also by 2-amyl-3-nitrophthalates which melt at 155°, and amyl phenylcarbamates which melt at 31° (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

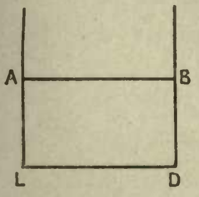


FIG. 4.

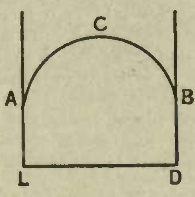


FIG. 5.

If, on the other hand, the solid which separates differs in composition from the fused mass, the melting-point curve will be either convex or concave. The former, Fig. 5, will occur when the concentration of the second enantiomorph in the separated solid is less, the latter, Fig. 6, when it is greater than in the fused mass. The curve in both cases will be a continuous one and reach its maximum or minimum at C when equal quantities of both enantiomorphs are present. A maximum, 91·4°, has been observed in the case of the carvoximes, the enantiomorphs melting at 72°; and a minimum in that of *d*- and *dl*-amyl carbamates (W. Marckwald and Nolda, Ber. 1909, 42, 1583).

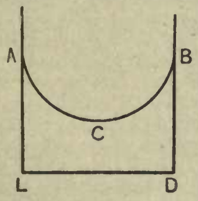


FIG. 6.

The above criteria in regard to the nature of an inactive substance only hold in the neighbourhood of the melting-points. At other temperatures, transformations may occur of a racemic compound to a pseudoracemic compound or a conglomerate or *vice versa.*

Solubilities of racemic compounds and mixtures. The phase rule may also be applied to the equilibrium between a racemic compound or mixture and its saturated solution in precisely the same way as to a mixed and double salt. A system consisting of a mixture of the dextro- and lævo- enantiomorphs in equilibrium with a saturated solution is a 3-component system and is invariant for a given temperature. The isothermal solubility curve of each will vary (increase or decrease) with each addition of the other enantiomorph until a maximum or minimum solubility point is reached when both are present in equal quantity, that is, when an inactive mixture is formed. If either enantiomorph is now added no change will result, for the solution is saturated in regard to each enantiomorph and neither will be dissolved. In Fig. 7, if the vertical represents the concentration of the lævo and the horizontal that of the dextro enantiomorph, the upper solubility curve *acb* represents that of a mixture (above or below the transition point of the racemic compound). The point *c* will lie on the line OB equidistant between the horizontal and vertical, since the two enantiomorphs possess identical solubilities. The solubility curve for the pure racemic compound will also cut the line OB either above or below *c*, depending on the transition temperature and, as in the former case, the point will be a maximum or minimum according to whether the solubility of the racemic compound increases or decreases in presence of excess of either enantiomorph.

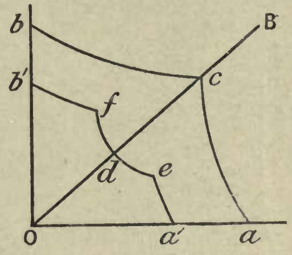


FIG. 7.

The curve *a′efb′*, in Fig. 7, represents the solubility curve for rubidium racemate, the transition point of which lies below that of the conglomerate. The addition of an excess of either enantiomorph will introduce a new phase and a new equilibrium will be established which will lie on *df* or *de* according to the enantimorph added; in other words, the solubility will be different from that of the pure racemic compound, and moreover some of the active component will pass into solution. Thus, by comparing the concentrations of the saturated solutions before and after addition of the enantiomorph, it would be possible to ascertain whether the original substance were a racemic compound or a conglomerate. Moreover, the addition of either enantiomorph to the solution of the racemic compound would produce an optically active solution which could be readily observed in the polarimeter. These facts have been demonstrated experimentally by Kendrick (Ber. 1897, 30, 1749) in the case of *r*-ammonium bimalate.

Partial racemism. The term is applied to those cases in which a double salt is formed, consisting of equal molecules of two active components which are not enantiomorphs. The phenomenon was first observed by Pasteur, who obtained crystals of a double salt of ammonium *d*-tartrate and ammonium *l*-malate. Another form of combination to which Ladenburg first applied the term *partially racemic* compound was observed by him in the case of quinine pyrotartrate, which forms three series of salts, from one of which the *d*-acid, from a second the *l*-acid, and from a third the inactive acid was separated. The quinine in the third case must therefore have united with the unresolved racemic acid or, what amounts to the same thing, a double salt of quinine *d*- and *l*-tartrate must have been formed.

An example of a similar kind was observed by Pope (Chem. Soc. Trans. 1898, 73, 902) in which the inactive base, *r*-tetrahydropapaverine, was found to form a double salt with *d*-tartaric acid. In the above cases, the solutions will be active and the two components will have different melting-points and solubilities. Consequently, neither melting-point nor solubility curves will be symmetrical. In the latter case the curve will resemble that of an ordinary double salt. If it lies beyond the transition point, the point of maximum or minimum solubility will not lie on OB and the addition of either enantiomorph to the solution of the original material would effect no change. Similarly if the solubility curve were drawn below the transition point it would have the form *a'efb'*, shown in Fig. 8, and three different solutions could be obtained corresponding to *e*, *d* and *f*, that is, the addition of either enantiomorph to the partially racemic compound would alter the concentration as in the case of the racemic compound.

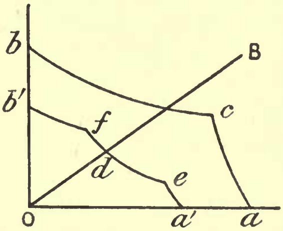


Fig. 8.

Racemic liquids. The question of the existence of racemic liquids has frequently been discussed. Ladenburg found that by mixing *d*- and *l*-conine a decrease of temperature of 1·4° was observed and concluded that the product was a racemic liquid. As the mixing of two enantiomorphs would produce no change of temperature, unless change of internal energy followed by combination of some kind had occurred, Ladenburg was probably correct in supposing that a racemic compound was formed; but the experiment does not prove that the whole product is racemic (A. Meyerhoffer, Gleichgewichte der Stereomeren, Leipzig, 1906). That such an equilibrium mixture of conglomerate and racemic compound can exist in a fused state follows from a study of the temperature-pressure curves of racemic and tartaric acid, the fusion curves of which must be continuous. There is nothing surprising in the fact that the magnetic rotations of ethyl tartrate and racemate are identical (Perkin, Chem. Soc. Trans. 1887, 51, 368) as this property is determined only by the number and kind of atoms. The same applies to specific rotation (Pope and Peachey, Chem. Soc. Trans. 1899, 75, 1117). The density of ethyl tartrate and racemate and other active and racemic liquids (such as conine and tetrahydroquinoline) are also identical. The same appears to be true of the boiling-point. Limonene and dipentene and active and racemic malic ester, however, show small differences of 1° or 2°. The solubilities of active and inactive liquid carvoxime in alcohol are the same.

The observation that the rate of decomposition of camphor carboxylic acid in acetophenone solution is 3 p.c. less when a mixture of *d*- and *l*-acids is used than when either is present alone seems to offer evidence of the existence of racemic compounds in the liquid state or in solution (Fajans, Zeitsch. physikal. Chem. 1910, 73, 25). J. B. C.

RACHITOL *v.* Synthetic drugs.

RACK-A-ROCK *v.* Explosives.

RADDLE. A kind of red ochre *v.* Reddle.

RADIOACTIVITY. I. The science of radioactivity dates from the year 1896, when H. Becquerel made the important discovery that uranium salts *spontaneously* emit radiations capable of affecting photographic plates and of penetrating considerable thickness of matter (Compt. rend. 1896). The radiation did not decrease with time, and its intensity was independent of the physical conditions to which the uranium was subjected. The radiations also produced phosphorescence in certain materials, such as zinc sulphide and ionised gases through which they passed. By an examination of various compounds containing uranium Mme. Curie was able to show that the intensity of the radiation depended only on the amount of uranium in the specimen examined, and not on its composition. The name *radioactivity* was given to the newly-discovered property of uranium. In 1898 it was shown independently by G. C. Schmidt (Wied. Ann. 1898, 65) and by Mme Curie (Compt. rend. 1898) that the property of radio-activity was shared by thorium compounds and minerals containing that element. A little later Mme Curie showed that the content of different minerals in radio-active material varied greatly, and that some minerals were even more active than metallic uranium. Such was the case with pitchblende from Joachimstal, and it therefore seemed that the radioactivity of this mineral could not be entirely ascribed to uranium. Further investigations by M. and Mme Curie led to the chemical separation of highly radioactive substances from pitchblende, with the result that two new radioactive elements, *polonium* and *radium*, were discovered (Recherches sur les Substances Radioactives, 2nd ed., Paris, 1904). A third radioactive element, *actinium*, was subsequently isolated from pitchblende by Debierne (Compt. rend. 1899 and 1900). The method of separating these elements from pitchblende consisted in subjecting the mineral to certain chemical reactions and examining with an electroscope the radioactivity of the products obtained. The method, in fact, was one of ordinary fractionation in which chemical tests were replaced by electroscope measurements. The three new radioactive elements polonium, radium, and actinium, are precipitated, respectively from uranium ores with bismuth, barium, and certain rare earths, notably thorium. Such precipitations formed the starting-point for the separation of these bodies, but as the new elements closely resemble the elements with which they are precipitated, their further purification was a matter of considerable difficulty. Ultimately, however, very active preparations of salts of all three elements have been prepared, and in the case of radium, in sufficient quantity and in a state of sufficient purity for atomic weight determinations to be made. In some early experiments Mme Curie found the value 225 for the atomic weight of radium, and in later experiments 226·2 (Compt. rend. 1907, 145). Thorpe has also made a determination, and gives the value 227 (Proc. Roy. Soc. 80, 1908). O. Hönigschmid (Wien. Akad. Anzeiger. 1911, 19, 1), from a series of concordant determinations in which from 0·6 grm. to upwards of 1 grm. of $RaCl_2$ were employed, found that Ra=225·95 (Ag=107·88 and Cl 35·457). The spark spectrum of radium has also been examined by Demarçay (Compt. rend. 1898, 127; 1899, 129; and 1900, 131) and others, and the flame spectrum by Giesel (Phys. Zeitsch. 1902, 3). Both spectra have been carefully studied by Runge and Precht (Annalen Phys. 1903, 10; 1904, 14). The spectrum of radium shows certain important similarities to those of magnesium, calcium, strontium, and barium, to which group of elements radium belongs. Pure metallic radium has been isolated by Curie and Debierne (Compt. rend. 1910, 151), and an amalgam of the metal is known (Coehn, Ber. 1904, 37).

Radioactive emanations. It was found that when measuring the ionisation produced by thorium, the results were greatly disturbed when air currents were set up in the vessel containing the thorium. These disturbances were traced by Rutherford to the fact that thorium salts continuously emit a temporarily radioactive gas, which he named an *emanation* (Phil. Mag. Jan. 1900). Similar radio-active gases have since been shown by Dom to be given off by radium (Abhandlungen der Naturforscherversammlung zu Halle, 1900), and a similar emanation has been found by Debierne from actinium (Compt. rend. 1903, 136). The activity of all these gases is not permanent, but falls off in geometrical progression with time, indicating that some change is proceeding which follows the same law as a monoatomic chemical reaction. The activity of the actinium emanation decays so quickly that after 3·7 seconds it has fallen to half its original value. The thorium emanation takes 53 seconds to lose half its activity, and the activity of radium emanation is much more permanent, falling to half value in 3·85 days. The properties of the emanations are in many ways analogous, but on account of the slow decay of its activity more is known about radium emanation than about that from thorium or actinium. The rate of evolution of the emanation from radium depends largely on the physical state of the radium salt. Thus, if very carefully dried, less emanation is evolved than when the salt is moist. A solution of a radium salt evolves emanation still more freely and by boiling can be completely deprived of the emanation contained in it. When the emanation has been expelled, the salt is said to be *de-emanated.* De-emanation can also be effected by heating a radium salt to about 800°. It thus appears that only a definite quantity of emanation can be extracted at any time from a given quantity of radium: but it is found that the radium gradually regains its power of emanating. After 3·85 days half the original amount of emanation can again be drawn off, and after the lapse of some weeks as much emanation can be collected as was originally extracted. While the radium is regaining its emanating power, the emanation gradually loses its activity, and it is found that at any time the sum of the activities of the emanation which has been separated from the radium and that which is unseparated is constant. The explanation of this fact will be seen later. Radium emanation can be collected in comparatively large quantity, so that its chemical and physical properties can be studied. It is a matter of great difficulty to purify the emanation from the other gases, but by special methods this can be done. By a somewhat indirect method it has been shown by Rutherford and Geiger that it should be possible to extract from one gram of pure radium 0·585 cubic mm. of pure emanation (Proc. Roy. Soc. 1908, 81). This value has been found by direct experiment to be correct by Ramsay and Soddy (*ibid.* 1903, 72) and Rutherford (Phil. Mag 1908). The nature of the emanation has been carefully studied, and it has been shown to behave in every way exactly as an ordinary gas. It can be condensed to a liquid by cooling, and its boiling-point is given by Rutherford and Soddy as −150° under ordinary conditions when mixed with air (*ibid.* 1903). When purified its condensation point rises with increase of pressure, and becomes −65° at atmospheric pressure (Rutherford, *ibid.* 1909). The emanation also diffuses as other gases, and dissolves in liquids, and Boyle has shown that it obeys Henry's law of solution (*ibid.* 1911). The spectrum of the emanation has been mapped by Rutherford and Royds (*ibid.* 1908). The value of the atomic weight of radium emanation can be predicted from theoretical considerations as 222. A direct determination by Gray and Ramsay gives 220 (Proc. Roy. Soc. 1911, 84). Chemically the emanation behaves as an inert gas, and seems to be monatomic and to belong to the argon family. The properties of thorium and actinium emanations have not been so fully studied, on account of the difficulty of obtaining sufficient quantities of these gases, but there is every reason to believe that they have similar properties.

The active deposits.—In an important investigation Curie has shown that bodies brought into the neighbourhood of radium themselves become temporarily radioactive, having acquired the property of emitting radiations even when removed from the presence of the radium (Compt. rend. 1899, 129). The bodies were said to have had radio-activity *induced* or *excited* in them. Analogous phenomena were discovered by Rutherford for thorium (Phil. Mag. 1900) and by Debierne for actinium. The activity so induced was soon shown to be transferred to the bodies made active by the emanations escaping from the radioactive sources. The activity produced was only temporary as with the emanations, but the rates of decay were different from those of the emanations and characteristic of the element inducing the activity. Subsequent experiments have shown that bodies made active in this way could be deprived of their activity by mechanical means such as rubbing on a rough surface, or, chemically, by immersion in hydrochloric or nitric acid. Also by strongly heating the surface, the activity was removed. It therefore appeared that induced activity is due to the deposition of radioactive matter; the name 'induced activity' has therefore been abandoned and replaced by the name *active deposit.* The decay of activity of the active deposits is complicated, and depends on the conditions of deposition, but after the lapse of some hours the activity decays in a geometrical progression with time, falling to half value in 26 minutes for radium, 36 minutes for actinium, and 10·5 hours for thorium.

The phenomena described show that the elements radium, thorium, and actinium spontaneously give rise to a number of different forms of radioactive matter with definite chemical and physical properties, and the processes involved seem to take place independently of external conditions. To explain these facts the theory has been put forward by Rutherford and Soddy, that radioactivity is due to the disintegration of the radioactive elements, and that the radiations emitted are the manifestation of this process (*ibid.* 1902). Thus, in the case of radium, the atoms are slowly but continuously breaking up, and at each disintegration of an atom an α particle is evolved, so that there is formed a new atom, the emanation, with a lower atomic weight possessing chemical and physical properties different from those of radium. The atoms of emanation in turn break up, giving rise to the active deposit. The latter has been shown to consist of a complicated mixture of products formed consecutively as the result of a series of atomic disintegrations. These are known respectively as radium A, B, C, D, E, and F. A mathematical theory, based on the above assumptions, has been worked out, and has been of the greatest service in analysing the complicated phenomena involved in radioactive transformations. In a simple transformation the activity falls off as a geometrical progression with time, and assuming that the ionisation produced is proportional to N, the number of atoms breaking up per second, we have the relation $N=N_0e^{-\lambda t}$, where N_0 is the intensity of the activity at the beginning and λ is a constant characteristic of the particular atom considered. Differentiating the above equation, it is seen that p, the rate of disintegration of the matter, is given by $p=\frac{dN}{dt}=\lambda N$ so that λ represents the fraction of the total number of atoms disintegrating per second. The quantity $\frac{1}{\lambda}$ is sometimes taken as defining the rate of decay of a radio-active element, and is called its *mean life.* It is more usual to define the rate of decay by the time taken for the number of atoms present to decrease to half their original number. This time τ is connected with λ by the relation $\tau=\frac{1}{\lambda}\log_e 2=0{\cdot}693\frac{1}{\lambda}$. This quantity is called the *time period* of the product. It must be understood that the above equations give a statistical representation of the phenomena, and are only true when the number of atoms involved is large compared with the number breaking up per second. In this case the laws of probability apply, but if the number of atoms is small, this is no longer the case. From a knowledge of the way in which a radioactive product decays, its rate of growth from a constant source of supply can be calculated. Thus, to take as an example, the case of radium which disintegrates so slowly that the number of atoms present does not vary sensibly over a short time. Suppose that the radium has been de-emanated, it is required to find the quantity of emanation present in the radium at any subsequent time. Let q be the number of atoms of emanation produced from the radium per second, and let N be the number of atoms present after a time t. Then $\frac{dN}{dt}=q-\lambda N$, where λ is the radio-active constant of the emanation; for the number of atoms of emanation disintegrating per second is given by λN. After a long time when the number of atoms of emanation formed equals the number breaking up, the emanation will have come into equilibrium with the radium; there will then be some definite number N_0 of atoms of emanation present. By integrating the above equation we get $N=N_0(1-e^{-\lambda t})$, since when $t=\infty$, $q=\lambda N_0$; for ultimately the number of atoms of emanation disintegrating becomes equal to the number formed from the radium. When this stage is reached a state of *radio-active equilibrium* is said to have been set up between the two products. It will be seen that the equation giving the rise of the number of atoms of emanation from de-emanated radium is complementary to that for the decay of the emanation, showing that the total number of atoms of emanation equivalent to a definite quantity of radium is constant, whether it is associated with the radium or has been separated from it. The processes which have been exemplified by the case of radium hold generally for all radio-active bodies, but the decay constants are different in every case. A general expression has been given by Bateman for the number of atoms of any product present at any time in a series of successive products if the number of atoms of each product present at some fixed time is known (Proc. Camb. Phil. Soc. 1910, 15).

The disintegration theory frequently gives a means of detecting new products and of estimating their radioactive constants; but it is often necessary to separate products from each other to examine them alone under simple experimental conditions. There are three ways of doing this. Firstly, by chemical means which can be exemplified by the first separation made by Crookes (Proc. Roy. Soc. 1900, 66). Uranium can be precipitated from its salts by addition of ammonium carbonate; the precipitate is, however, dissolved by excess of the reagent, but a strongly radioactive light brown residue containing iron and other impurities is left in suspension. The activity decays to half value in 22 days, showing that the residue contains a product which has been called uranium X (*q.v.*). There are many other cases of such chemical separations which might be cited. A second method of separating products is by fractional distillation. Most of the radioactive products boil at high temperatures, though there is evidence in many cases of volatilisation even at ordinary temperatures. By heating to a suitable temperature a separation of two or more products can therefore be effected. A third way of separating successive radio-active products is by the method of *recoil.* When an atom emits an α-particle, the residual atom constitutes the product next in the radioactive series. Now, since the α particle possesses considerable momentum, the residual atom receives a shock sufficient to carry it some distance in a direction opposite to that in which the α-particle is travelling before it is brought to rest by collisions with molecules of the medium through which it is moving. At atmospheric pressure an atom will travel about 0·1 mm. through air. Take, for example, the case of radium B formed from radium A. The velocity of the α particle from RaA is $1{\cdot}77 \times 10^9$ cms. per second, and since the α particle is a charged atom of helium, its atomic weight is 4. The atomic weight of RaB is 214, so that from the laws of momentum the atom of RaB must be travelling at the rate of $3{\cdot}3 \times 10^7$ cms. per second immediately after the expulsion of the α particle. Now, it has been shown by Russ and Makower (*ibid.* 1909, 82) that the recoiling atoms travel considerable distances through a vacuum, and can be collected on a surface placed to receive them. In this way RaB may be completely separated from RaA, and can be obtained in a state of high purity. A more convenient way of effecting the separation was discovered independently by Hahn and Meitner (Verh. der Deutsch. Physik. Ges. 11, 3), who give a method of avoiding working in *vacuô*. To take the same example as above, if a plate coated with RaA is charged positively and a second negatively charged surface is brought near the first plate, the recoiling atoms of RaB are collected on the negative surface. Hahn and Meitner have in this way isolated several new products, amongst which may be mentioned thorium D and the product radium C_2, which will be mentioned later. Later experiments by Russ and Makower and Makower and Evans have shown that a 'recoil-stream' of atoms of RaB is positively charged, and can be deflected when passing through an electric or magnetic field (Phil. Mag. 1910). The experiments show that the recoiling atoms move with a velocity of $3{\cdot}23 \times 10^7$ cms. per second, and each carry a unit charge of electricity. A rough determination of the atomic weight of RaB is also made which agrees with the value predicted by theory. The product RaC_2 has been further studied by Fajans (Physikal. Zeitsch. 1911, 12), who shows that RaC_2 is formed only in very small quantity from RaC_1. From recent experiments it appears that on breaking up, an atom of RaC_1 usually gives rise to RaD, but occasionally an atom of RaC_2 is formed instead. RaC_2 is not intermediate between RaC_1 and RaD, but constitutes a side branch. Another case of a side branch has recently been discovered by Antonoff, who finds that uranium can produce a product named UrY in small quantity as an alternative to UrX (Phil. Mag. 1911).

A general survey of the known radioactive elements and their connection with each other will now be given. No connection has yet been found between thorium, radium, and actinium and their products of disintegration. It seems nevertheless probable that radium and actinium are related in some way as yet not understood. The element polonium has been shown to be a disintegration product of radium and to be identical with RaF. A definite relation has been established between uranium and radium. Just as is the case with all radio-active elements, radium is constantly disintegrating. It can easily be calculated that the time period of radium is about 2000 years, so that it is difficult to understand how this element can have persisted through geological ages in minerals, unless it is being supplied from some source. It was suggested by Rutherford and Soddy that the supply was derived from uranium, and this has since been proved to be the case by the experiments of McCoy (Ber. 1904, 37), Boltwood (Phil. Mag. 1905), and Strutt (Proc. Roy. Soc. 1905, &c.), who have shown that the ratio of the amount of radium to that of uranium in old minerals is nearly always constant. This is exactly what would be expected if radium were produced from uranium and sufficient time had elapsed for radioactive equilibrium to be set up. Experiment has, however, failed to reveal the production of radium from uranium, although the transformation should be proceeding sufficiently rapidly to be detected. Soddy has shown that not more than $\frac{1}{10000}$ of the amount of radium to be expected is formed from a solution of uranium (Phil. Mag. 1905). The explanation of this discrepancy has been given by Boltwood, who has isolated a product of very long period between uranium and radium, named by him *ionium* (*q.v.*) (Amer. J. Sci. 1906, 1907, 1908).

In the thorium series, some very active products have been separated by Hahn, who has shown that thorium is immediately followed by three products besides ThX before the emanation is reached. These have been called mesothorium 1 and 2 and radiothorium respectively. Hahn has prepared specimens of mesothorium of activity nearly equal to that of radium. A complete list of the known radioactive elements is given in the table, together with important data relating to them. In the case of products which emit α-rays the ranges in air at atmospheric pressure and 0° are given. The analogy between the three emanations and the products immediately following them is very striking.

In the table lead is given as the last disintegration product of uranium immediately following RaF. Though there is no direct proof that this is the case, all exisiting evidence points to this connection between uranium and lead. Direct proof of the point could only be obtained by obtaining polonium in sufficient quantity to test whether lead is produced from it, but this has not yet been done. The indirect evidence upon which the conclusion is based is of two kinds. In the first place the work of Boltwood has shown that lead always occurs in radioactive minerals in such amount as is to be expected if it has been formed from uranium (Amer. J. Sci. 1905, 1907). The conclusion drawn by Boltwood is also supported by the following theoretical consideration. Polonium (RaF) is formed from radium as the result of a number of transformations involving the loss of seven α particles. Now, since the atomic weight of uranium is 238·5, and that of each α-particle is 4, the atomic weight of polonium should be 210·5. Now, polonium emits α particles, so that the atomic weight of the next product should be 206·5, a value which is very close to the known atomic weight of lead.

Emission of heat by radio-active bodies. Curie and Laborde were the first to show that radium is always at a temperature above surrounding bodies (Compt. rend. 1904, 136). Many experimenters have since measured the heat emitted by radium, and the latest determination by Schweidler and Hess gives the value 118 calories per hour per gram of radium (Wien. Ber. 1908). Rutherford and Barnes have made a detailed examination of the heat emitted by the products of radium separately, and have shown that the heat generated is derived from the energy of the α particles emitted (Phil. Mag. 1904). The β and γ rays seem to be responsible only for a very small part of the heat evolved. Measurements on other products have confirmed the view that the heat developed in radio-active changes is proportional to the energy of the α particles. It will be noticed that the emission of heat by radium is very large, being sufficient to melt its own weight of ice in 40 minutes. This evolution of energy during radio-active changes may be taken as indicative of the enormous stores of energy which must be contained within the atoms.

Uranium Series.			Thorium Series.			Actinium Series.		
Product.	Period.	Radiation.	Product.	Period.	Radiation.	Product.	Period.	Radiation.
Uranium	6×10^9 years	α (2·58 cm.)	Thorium	3×10^{10} years	α (2·58 cm.)			
UrX	24·6 days	β and γ	Meso Th_1	5·5 years	—			
(UrY)	1·5 days	β (α ?)	Meso Th_2	6·2 hours	β and γ	Actinium		
Ionium	2×10^4 years ?	α (2·84 cm.)	Radio Th	737 days	α (3·67 cm.)	Radio Ac	19·5 days	α (4·55 cm.) β
Radium	2000 years	α (3·13 cm.) β	ThX	3·7 days	α (5·7 cm.) β	AcX	10·5 days	α (4·17 cm.)
Ra emanation	3·85 days	α (3·94 cm.)	Th emanation	53 secs.	α (5·5 cm.)	Ac emanation	3·9 secs.	α (5·40 cm.)
RaA	3 mins.	α (4·50 cm.)	ThA	0·14 sec.	α	AcA	0·002 sec.	α (6·16 cm.)
RaB	26·7 mins.	β and γ	ThB	10·6 hours	β	AcB	36 mins.	β
RaC_1	19·5 mins.	α (6·57 cm.) β	ThC_1	55 mins.	α (5·0 cm.)	AcC	2·15 mins.	α (5·12 cm.)
(RaC_2)	1·4 min.	β	ThC_2	?	α (8·6 cm.)			
RaD	16·5 years	—	ThD	3·1 mins.	β	AcD	4·71 mins.	β
RaE	5 days	β						
RaF (Polonium)	140 days	α (3·58 cm.)						
Lead ?								

The figures in this table show a certain relation between the period p of a substance emitting α rays, and the range r of those rays. Rutherford was the first to draw attention to the existence of such a relation, pointing out that in general p was large when r was small (Phil. Mag. 1907). Geiger and Nuttall have made fresh determinations of several ranges which had previously been somewhat uncertain; these have been used in the construction of the table (*ibid.*, 1911). They have taken the opportunity to re-examine the relation between p and r and find that for the radium series, and also for the actinium series, p and r are connected by the relation $rp^a = b$. Here a and b are constants, the former being the same for both series. The figures for the thorium series have not yet been completed. If the relation can be relied on, a very interesting result appears. It can be shown that the life of a substance emitting rays of short range, say 1 cm. would be so long, and therefore its transformation so slow, that its activity would be beyond the limits of detection by present methods. W. M.

II. This section deals with the phenomena attending the passage of α-, β-, and γ-rays through matter.

It is convenient to divide them into two parts: (i.) those referring to the action upon the rays; (ii.) those referring to the action upon the matter.

Further subdivision is convenient in respect to the phenomena of part (i.). The experience of an α-, a β-, or a γ-ray as it flies across an atom may be considered under three heads: (*a*) loss of energy, (*b*) deflection, (*c*) transformation or replacement. The α particle's experiences are mostly under (*a*): it is only slightly liable to scattering (*b*), and not at all to change of form (*c*). The β particle is very liable to deflection, which often makes its loss of energy difficult to detect, and it is liable to transformation into a γ-ray—the X-ray may be included as a form of γ-ray—especially if its velocity is not more than about one-third of that of light. The γ-ray (or X-ray) appears to suffer no loss of energy, and is somewhat liable to scattering; the most interesting and important event in its history is the transformation of its energy into that of a β-ray.

The most obvious of the phenomena to be included under (ii.) are heating, photographic action, phosphorescence, ionisation. The last three are used as indicators of the action of the rays.

General considerations.—In all cases known the phenomena of part (i.) are independent of physical and chemical conditions. For example, the probable loss of energy of an α particle in going through a definite small volume containing an atom does not depend on whether the atom is part of a hot body or of a cold body, of a solid or of a gas, of a simple molecule or of a complex one.

On the other hand, some of the phenomena of part (ii.) are not quite so simple. The number of ions which can be extracted from a gas after an α-particle has passed through it depends somewhat upon molecular association.

The α- and β-rays are really projectiles of very small mass, but of enormous speed. It would appear that the γ-ray (and the X-ray which has similar properties) may also be reasonably and usefully considered as a projectile. In the case of any of these forms of radiation small entities, quanta, or corpuscles are hurled against matter with relative speeds far exceeding those of the thermal agitation of a gas at any temperature yet realised. The results are peculiar, as might be expected. In particular the atoms are no longer impenetrable, but are traversed with the utmost freedom; and the actions and reactions between the projectiles and the atoms are of the greatest interest, affording glimpses of the atomic constitution from an entirely new standpoint.

We now take the three radiations in turn.

The α-ray.—The almost universal presence of helium in radioactive minerals early suggested the nature of the α-particle. A simple verification has been given by Rutherford and Royds (Phil. Mag. 1909). Radium emanation is enclosed in a glass tube with very thin walls, through which α radiation can pass. Outside the tube is an evacuated space, which shows no trace of the helium spectrum when sparked through immediately after the preparation of the tube. In a few days, however, the helium lines are strongly shown. In control experiments, when the inner tube is empty, and even when it is filled with helium, there is no such effect. It is clear that the emanation has shot helium through the glass.

Rutherford has determined the velocity of the α particle and the ratio of its charge to its mass by observing the effect of electric and magnetic fields upon its flight (Phil. Mag. 1906). The latter quantity he finds to be nearly 5×10^3, which shows that the α particle being a helium atom must carry twice the unit charge. The velocity will be considered later.

Since the α particle is very little scattered by the matter through which it passes, its path is almost exactly a straight line. It spends its energy as it goes, and, having spent it, comes to comparative rest at a certain distance from the starting-point, which distance is called the range. The range varies with the initial speed and with the nature and density of the gas traversed. It was first found, in the case of the α-rays of radium, by means of apparatus represented in the diagram (Fig. 1). A very thin layer of radium is placed on a plate RR. The α-rays stream upwards in all directions, but only those which proceed almost vertically succeed in passing through the set of tubes, TT. These are made of thin copper foil 1 cm. long and 2 mm. wide; the bundle contains about 150 of them. The α-rays which strike the walls of the tubes are embedded there. The rest stream upwards, ionising the gas; if they reach the gauze BB, and enter the ionisation chamber between BB and AA, then ionisation occurs in the chamber also, and is detected in the usual way. The lower gauze, CC, is connected with the earth, and the field between BB and CC protects the ionisation chamber from the intrusion of ions from below. The radium is gradually raised towards the chamber and the current measured for different positions; the 'ionisation curve' is thus obtained (Fig. 2) (Bragg and Kleeman, Phil. Mag. 1905). This curve is interpreted as follows. The small readings above A are due to the action of β- and γ-rays.

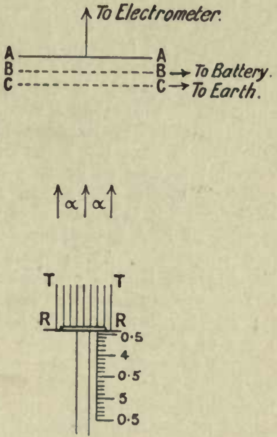


FIG. 1.

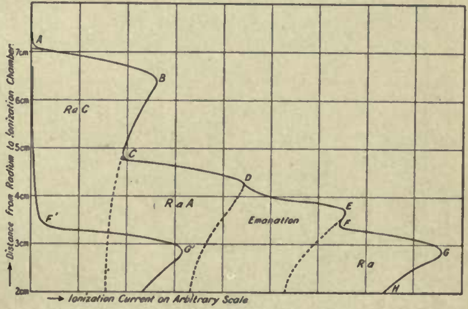


FIG. 2.

The sudden setting in of current at A, 7·14 cm. from the origin, implies that this is the furthest point of penetration of the α-rays. This distance is termed the range of the α particle in question. It is 7·14 cm. in air at a pressure of 76 cm. and a temperature of 20°. The range at any other pressure (P) and absolute temperature (T) is $7{\cdot}14 \times (76/P) \times (T/293)$. The slope, AB, is due to the fact that all the α-rays do not reach quite the same distance from the radium; the turn at B shows that at 6·5 cm. all the rays—of this stream—now make their way into the chamber. The gradual bend back, BC, implies that the α-particle is more effective as an ioniser as it slows down. The sudden break out again at C (4·84 cm.), shows that the chamber is now within range of a second stream of α-particles of shorter range than the first, and the portions DE and FG show that there are yet two other streams of still less range. When the radium layer is taken out, heated to a bright red heat and replaced in the apparatus, the middle parts of the curve CD and DE are found to have disappeared, and in an hour or so the top part AB has disappeared also, the curve therefore reducing to F′G′. Now it is known that the heating has driven off the emanation, and the RaA must have quickly followed the source of its existence. We conclude that the α-stream of least range (3·50 cm.) is due to radium itself, and that of greatest range is due to RaC. By separate experiment it is shown that the range of the α-particle of RaA is the longer of the two intermediate quantities, 4·84; and that the other, 4·23, belongs to the emanation. Each of the radioactive substances has thus its own range; and further, since the four steps of the curve are of exactly the same width, the rate of emission of particles from each product is the same, which is in agreement with Rutherford and Soddy's theory of radioactive change.

The ranges of the α particles of other substances can generally be found in similar fashion: difficulty arises only in the case of those which radiate weakly.

When a thin sheet of uniform material is placed over the tubes TT, so that the α particles must go through it, each particle loses a definite amount of its range, and the ionisation curve is correspondingly lowered (Fig. 3). The exact resemblance of the new curve to the old shows that the particles have lost neither in number nor in direction, so that they must have passed through all the atoms they have met in going through the sheet; the helium atom has freely penetrated the silver atoms. On comparing the effects of sheets of different materials the remarkable result appears that the masses of equivalent sheets (per cm.^{2}) are proportional to the square roots of the atomic weights of the substances of which they are composed. We may define the 'stopping power' of an atom as the probable loss of range which an α particle experiences in passing through a small volume containing only that atom, compared with the similar probable loss when some standard atom is substituted. We may conveniently take an imaginary air atom as standard (at. wt. = 14·4): the table on the next page gives the values of the stopping powers (s) of some molecules relative to the imaginary air molecule. The stopping power of a molecule is the sum of the stopping powers of the atoms of which it is composed; *e.g.* the stopping power of N_2O is to that of C_6H_6 in the proportion $2\sqrt{14}+\sqrt{16}$ to $6\sqrt{12}+6\sqrt{1}$ or 0·43. Experiment (*see* table below) gives 0·44.

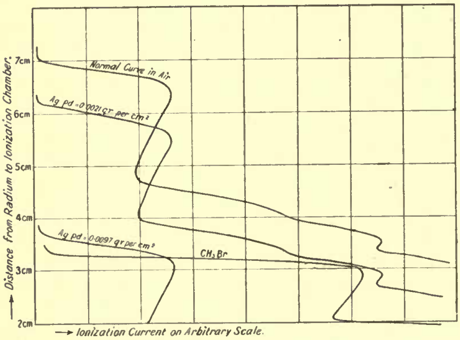


FIG. 3.

The stopping power of a gas is found by comparing the range of the α particle in the gas with the range in the air. An atom or molecule has the same stopping power, no matter whether it is part of a solid or of a gas.

The α particle is, as already mentioned, liable to deflection in passing through the atom. But the effect is small and unimportant except when its velocity becomes small. The remarkably rectilinear path of the particle has been beautifully illustrated by C. T. R. Wilson, Proc. Roy. Soc. 85, 285, and 87, 277. A chamber containing damp air is for a moment subjected to the action of the rays, and is immediately afterwards chilled by a sudden expansion of the air. Fog settles on the ions left along the track of the particle; Fig. 4 is a reproduction of a photograph of the event. The sharp lines belong to α particles which went by the instant before the expansion; the more diffused lines to those that were shot out a little earlier so that the ions have had time to spread somewhat.

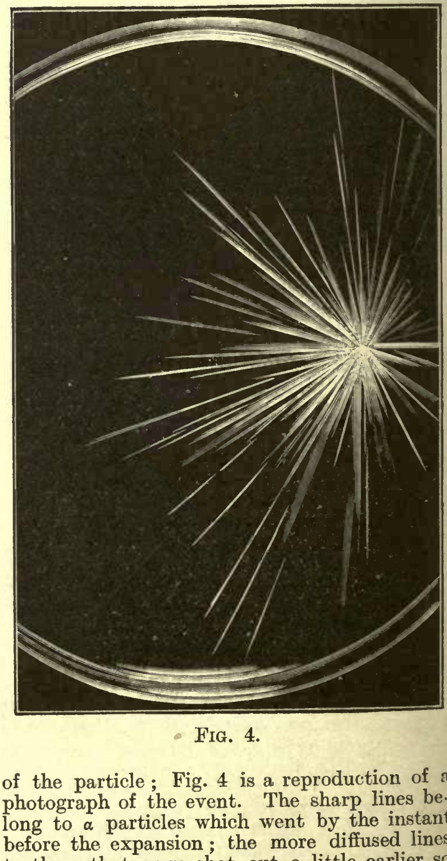


FIG. 4.

The scattering of the particle has been investigated by Rutherford and Geiger by the 'scintillation' method. When a stream of particles strikes a phosphorescent screen, such as zinc sulphide, the blow of every particle causes a momentary sparkle, and the numbers falling on any particular portion of the screen can be counted under the microscope. The apparatus is shown in Fig. 5 (Geiger, Proc. Roy. Soc. 83, 493). Some emanation is for a time compressed in the conical opening of the tube at A, and is then withdrawn. The active deposit which it leaves behind shoots α particles down the exhausted tube through small openings at D and E, and these fall on the phosphorescent screen at S. Screens can be put at E or on R, and the consequent scattering is then observed. It is very small. When, for example, the α particle passes through 20 gold leaves weighing about 3·5 mmg. per cm.^{2} the most probable angle of deflection is only 1° 40′. Comparing different substances, the most probable angle of deflection is proportional to the atomic weight. The scattering also depends on the velocity, increasing rapidly as the particle slows down, and being to a first approximation inversely proportional to the cube of the velocity. Near the end of its path, therefore, the particle may experience some very violent deflections; finally, it settles down to the usual movements of a gas atom.

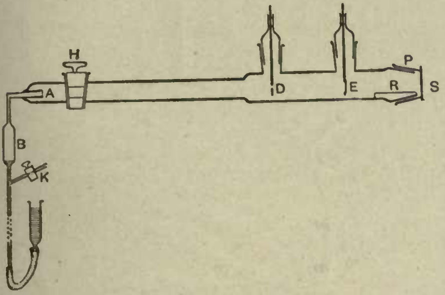


FIG. 5.

By the scintillation method, and by a method of intensifying the ionisation effect of the single α particle, Rutherford and Geiger have determined the rate at which radium emits α particles. Having found also the total charge of electricity conveyed by these particles, they have determined the charge carried by each one (Proc. Roy. Soc. 81, 141, 162). They give the following results:—

Charge (e) carried by the hydrogen atom in electrolysis $=4{\cdot}65\times10^{-10}$ E.S. unit.

Charge carried by the α-particle $=9{\cdot}3\times10^{-10}$ E.S. unit.

The value of Ne, where N is the number of hydrogen atoms in 1 grm. of hydrogen, being known from electrolysis, it is readily found that $N=6{\cdot}2\times10^{23}$, that the mass of the hydrogen atom is $1{\cdot}61\times10^{-24}$grms, and that the number of molecules per c.c. of any gas at standard pressure and temperature is $2{\cdot}72\times10^{19}$.

Rutherford and Hahn have measured the velocities of the α particles of various substances (Phil. Mag. 1906) as follows: RaC $2{\cdot}06\times10^9$; RaA, $1{\cdot}77\times10^9$; polonium, $1{\cdot}73\times10^9$ ThC, $2{\cdot}27\times10^9$.

Geiger has shown that the initial velocity is connected with the range by the formula $v^3=aR$ (Proc. Roy. Soc. 83, 505).

In order to explain the deflection of the α particle by the atom, it is necessary, according to Rutherford (Phil. Mag. 1911), to suppose that each atom possesses a nucleus of electrical charge ne, where e is the unitary electrical charge and n is a number of the order of half the atomic weight, and proportional to that weight. For instance, if n be set equal to 100, the scatterings of the α particles observed by Geiger in the case of gold are in very good accordance with calculations based on this theory. On the vast majority of occasions, when an α particle goes through an atom it does not go near enough to the central charge to suffer serious deflection. When a stream of α particles is hurled against a gold plate, only one in each eight thousand is returned. It will be seen that the scattering of the β particles is also explained by Rutherford's hypothesis.

Of the effects which the α particle exerts upon the matter which it traverses the most easily investigated is the ionisation. It is curious that molecular association is not quite without influence upon the total ionisation which a given α particle produces, although it does not count in the calculation of the energy which the particle spends. The total ionisation is greater ('k' times greater) in most gases than in air. We may define a quantity called the molecular ionisation, which will represent the probable ionisation produced when an α particle crosses a given volume containing the molecule in question. This is obtained by multiplying k by s, the stopping power, since the greater the latter quantity the fewer the molecules that contribute to the total ionisation. The molecular ionisation is not quite an additive quantity. It is roughly proportional to the volume of the molecule. A few values of these constants are here given as illustrations:—

TABLE I

	k.	s.	ks.
Air . .	1·00	1·00	1·00
CO_2 . .	1·03	1·50	1·55
C_2H_2 . .	1·26	1·118	1·40
C_2H_4 . .	1·22	1·32	1·61
C_2H_6 . .	1·30	1·51	1·96
CH_4 . .	1·17	0·86	1·005
H_2 . .	1·00	0·24	0·24
He . .	—	0·201	0·22
Ar . .	—	0·95	1·24

For the values of k and s in other gases, *see* Bragg (Phil. Mag. 1907), Metcalfe (*ibid.* 1909), Taylor (*ibid.* 1911).

The β ray. The direction of deflection of the β ray in a magnetic field shows at once that it is a negatively charged body. Measurements of the deflections in crossed electric and magnetic fields (*e.g.* those of Kaufmann, Annalen Physik, 1906 [iv.], 19, 487) give the velocity (v) and the ratio of charge to mass (e/m). The latter quantity is the same as that of the electron, unless the speed is very great, and this practically identifies the β ray with the electron. The ratio is found to diminish as the velocity approaches that of light. The diminution is such as would be expected, on electro-magnetic theory, if the mass of the electron were wholly electro-magnetic. When $v=0{\cdot}94$V, where V=

the velocity of light, $e/m=0{\cdot}63\times10^7$ E.M.U.; when $v=0{\cdot}59V$, $e/m=1{\cdot}68\times10^7$. The β-rays of radium vary considerably in speed, some moving with a velocity little less than that of light.

In its movement through matter the β particle is much more liable to deflection than the α particle, and a stream of particles directed against a material screen loses rather by deflection of individuals than by general slowing down. The degree of penetration depends very largely on the speed. The β ray of radium can sometimes traverse a few metres of air, whilst 'cathode rays' of one-third the speed are nearly all absorbed in two or three millimetres. The movements and penetrations of β-rays are beautifully shown in some early experiments by Becquerel, which are illustrated in the accompanying figures. Fig. 6 is diagrammatic, and shows how the β-rays from a small quantity of radium are swung round in circles by a magnetic field through openings in certain screens. The rays skirt a photographic plate in the plane of the paper, and leave records of their paths. Fig. 7 shows what happens when a sheet of Al 0·1 mm. thick is placed over all the holes in the outer screen, so that the β-rays have to go through it. It will be observed that the faster β-rays at least—those moving in the circles of least curvature—retain their direction after passing through the layer. The scattering may also be observed by measuring the ionisation which the deflected rays produce in chambers suitably placed. When a stream is directed against a plate, the number of rays swung round so far as to re-emerge on the side on which the stream is incident increases rapidly with the atomic weight of the substance of the plate (McClelland, Roy. Dublin Soc. Trans. 1905 *et seq.*). The central charge or nucleus which Rutherford found necessary to explain the deflection of the α-particle gives a satisfactory explanation of the deflections of the β-particles also.

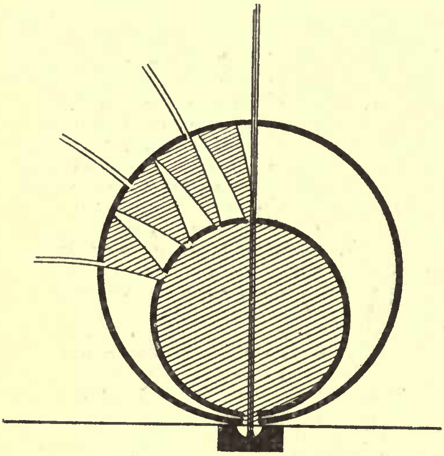


FIG. 6.

From Becquerel's experiment and from many others, such as, for example, those of Madsen (Phil. Mag. 1909), it appears that a penetrating β-ray must generally traverse thin sheets of metal without any serious deflection, and the few which have been turned aside out of the main stream have only been deflected once. Thus observations of the distribution of the scattered rays give information as to the probable result of the encounter of a single electron with a single atom. Information of this kind is most desirable as helping to a knowledge of atomic constitution.

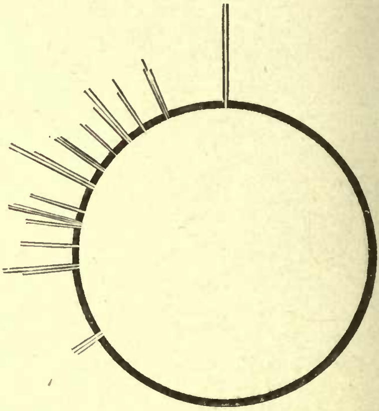


FIG. 7.

The β-particle suffers a loss in speed in going through matter, but for a long time the loss was unobserved; it is difficult to measure with certainty because the scattering effects mask it. W. Wilson found (Proc. Roy. Soc. 84, 141) that the energy of a β-ray fell off in proportion to the amount of matter penetrated. An initial velocity of $2{\cdot}85\times10^{10}$ cm./sec. was reduced to $2{\cdot}80\times10^{10}$ by a screen of aluminium 0·5 mm. thick, to $2{\cdot}70\times10^{10}$ by a screen 1·0 mm. thick, and to $2{\cdot}25\times10^{10}$ by a screen 1·7 mm. thick. The scattering of the β particle increases very fast as its speed decays, and the power of penetrating material is affected more by chance of scattering than by loss of velocity. The β particles of the highest speed named above are seven times as penetrating as those of the lowest, chiefly on account of differences in the liability to scattering. The loss of velocity depends on the nature of the matter in somewhat the same fashion as in the case of the α-rays. The loss in passing through an atom is proportional to $w^{2/3}$, where w is the atomic weight; in the case of the α-particle, it is proportional to $w^{1/2}$, as already said. The whole of this may be compressed into the statement that in a substance of small atomic weight like aluminium a particle projected with given velocity reaches a greater distance from the origin (measured by mass penetrated) than it does in a substance of large atomic weight like platinum. But it really pursues a longer path in the latter (again measured by amount of matter traversed), only the path is much more broken and irregular.

Rutherford has shown (Phil. Mag., Oct. 1912) that the heterogeneous β-radiation from a substance like RaC consist of a group of homogeneous β-radiations. The energy of each member of a group is characteristic of that group. The difference between the energies of any two groups is closely connected with the energy required to excite the X (or γ) radiation characteristic of the radioactive substance, a quantity which is found by extrapolation from X-ray measurements with substances of lower atomic weight. This work also suggests the interchangeability of the energy of the β- and the X- or γ-ray, with the additional hypothesis that in the process of expulsion from the radioactive atom, one β-ray may give rise to more than one γ-ray, and *vice versâ*.

The ionisation produced in a gas by a stream of β-rays varies with the nature of the gas in much the same way as in the case of the α-rays (Kleeman, Proc. Roy. Soc. 79, 220). A few examples of molecular ionisations by α-, β-, and γ-rays are given side by side in the following table:—

TABLE II

	α	β	γ
Air	1·00	1·00	1·00
CO_2	1·59	1·60	1·58
C_2H_4O	2·14	2·12	2·17
$CHCl_3$	4·08	4·94	4·93
C_2H_5I	4·00	5·90	6·47

Lastly, reference must be made to the chance of transformation of β-radiation. It is rarely observed in the case of the swift electrons emitted by radioactive substances; the only case known is that given by Gray (*ibid.* 85, 131), who found that the β-rays of RaE, which are very absorbable, produced γ-rays in substances on which they fell. In the case of the slower electrons of the vacuum tube, the effect is common enough, being in fact that on which the production of X-rays is based.

The γ-ray.—When γ-radiation, or X-radiation which differs from γ-radiation in degree, but not in kind, meets with matter there is a production of β-radiation. The energy of the γ-radiation is transformed into energy of the other. Since β-rays produce phosphorescence, ionisation, and photographic action, it may be assumed that these effects, when they accompany the passage of γ- or X-rays, are really the direct result of the β-rays, into which the γ- or X-rays are transformed. The laws of the transformation become the first object of investigation. It appears that in the first place the speed of the β-ray produced in this way increases with the penetrating power of the γ-ray; but it is independent of the intensity of the γ-ray and of the nature of the matter in which the transformation takes place. Secondly, the initial direction of motion of the β-ray is more or less a continuation of that of the γ-ray; more so, the more penetrating the latter ray, and the lighter the atom of the material. These facts suggest that the energy of each β-ray comes from the store of energy of one γ-ray, which in disappearing hands on energy and direction of motion to the electron which takes its place. The γ-ray energy must therefore be contained within a very small compass, and must keep its form and magnitude unchanged as it moves, so that when the fatal encounter takes place in some atom the energy may be ready, undiminished, for transformation. It is a striking fact that the energy of the cathode ray, which produces the X-ray in the vacuum tube, is nearly the same as that of the cathode ray, which the X-ray produces, so far as present experiment can tell. It is at any rate not much greater. It may be concluded that the electron in the tube is there replaced by, or transformed into, an X-ray, and that the latter, if it succeeds in passing through the tube wall, is available for retransformation into a moving electron. The history of a γ-ray or X-ray, or of the energy carried by the ray, is therefore the history of an individual quantity of energy manifest now in one form, now in its alternative. As a γ-ray, the quantum must spend nothing as it goes through matter, since it has to carry its energy intact to the place of transformation; when it is in the β-ray form it is much liable to scattering, and liable also to diminution of energy, and interchanges proceed until all the energy has been spent (Corpuscular theory of X- and γ-rays, Phil. Mag. 1910). An experiment of C. T. R. Wilson's illustrates this deduction; a fog is made to settle on the ions produced by the passage of X-rays through the air, and it will be observed (Fig. 8) that the ionisation lies on shot irregular lines two or three millimetres long distributed in a promiscuous manner through the gas. These represent the tracks of the slow-moving β-rays into which X-rays are transformed by the atoms of the gas, and the effect realises anticipation very closely.

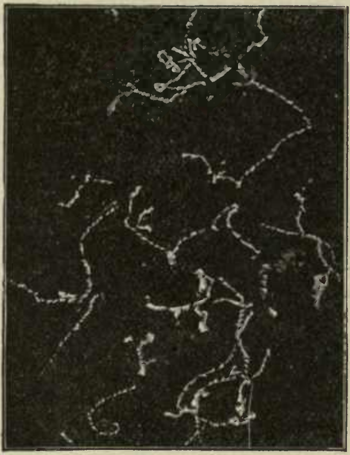


FIG. 8.

The energy of the X-ray must lie between that of the cathode ray which makes it and that of the cathode ray which it makes. The two extremes being not far apart and possibly identical, the energy of the X-ray is a sufficient and proper definition of its quality, and is a more fundamental basis of definition than the absorption in some material taken as standard. From analogy it may be supposed that the same applies to the γ-ray.

The deduction stated above, viz. that the X-ray produces no ionisation by direct action, but only through the agency of the β-ray, has been tested by Bragg and Porter (Proc. Roy. Soc. 85, 349), and found to be true within errors of experiment.

The 'absorption coefficient' of γ-rays in any substance is really a measure of the proportion that are converted into β-rays in crossing a given stratum of that substance. If this proportion is put equal to λdx, where dx is the product of the thickness of the stratum and its density, then for most substances λ is nearly 0·040 in the case of the γ-rays of radium and 0·047 in the case of the γ-rays of uranium. For lead and other substances of high atomic weight, it is a little larger (*see*, for example, Soddy and Russell, Phil. Mag. 1910).

The scattering of the γ-ray in its passage through matter has been examined by several workers, *e.g.*, Madsen (Trans. Roy. Soc. of South Australia, 1908) and Florance (Phil. Mag. 1910). The latter states that if a stream of heterogeneous γ-rays from radium is scattered in passing through matter, that which is less penetrating is more scattered than that which is more penetrating. The analogous effect occurs in the case of the β-rays.

The nature of the γ-ray is still a matter of discussion. The æther pulse theory supposes the γ-ray to be the disturbance in the æther which must occur when a β-ray is discharged from the atom. Such a supposition links closely together γ-rays, X-rays, and light as variants of one form of radiation, and is based on the many points of resemblance between the three. Amongst resemblances of especial interest may be mentioned Barkla's discovery that X-rays can be polarised in a manner suggestive in some degree of the polarisation of light, and the remarkable experiments of Friedrich, Knipping, and Lane, which are best explained on the supposition that X-rays can be reflected in such planes within a crystal as are rich in atoms. The pulse theory is, however, unable to give a ready explanation of the interchangeability of X-ray and β-ray energy.

If the ionisation in a gas traversed by γ-rays is due to the β-rays produced by the γ-rays in the walls and in the gas, the 'ionisation of gases by γ-rays' is really an ionisation by β-rays. In the fourth column of Table II. some of the values found for the ionisation of gases by γ-rays are set out, and may be compared with the values in the third column (Kleeman, Proc. Roy. Soc. 79, 231).

W. H. B.

RADISH, *Raphanus sativus* (Linn.). Several varieties have been distinguished, *e.g.* *R. s. griseus*, *R. s. radicula*, and *R. s. tristis*. The first produces seeds rich in oil, the second yields very small edible tap roots, whilst the third is valued for its relatively large tap root. The roots of all possess the well-known pungent flavour due to allyl *iso*-thiocyanate. König gives, as the composition of the edible portions of the roots—

	Water	Protein	Fat	Sugar	Other N-free ext.	Crude fibre	Ash
R. s. tristis .	86·9	1·9	0·1	1·5	6·9	1·6	1·1
R. s. radicula	93·0	1·2	0·2	0·9	2·9	0·8	0·7

According to Saiki (Zeitsch. physiol. Chem. 1906, 48, 469), radishes contain a powerful diastatic ferment, which can be obtained in the form of a yellowish-white, somewhat hygroscopic powder. Little or no starch is present in the root under normal conditions, but when the plants are watered with a solution containing from 4 to 10 grms. of sodium chloride per litre, the roots contain considerable quantities of starch (Lesage, Compt. rend. 1891, 113, 373). Boric acid has been found in radishes (Gessend, Ann. Agron. 1891, 17, 352). By distilling an aqueous extract of *Raphanus niger* (Mill.) (*R. sativus*), Morcigne (J. Pharm. Chim. 1896, 4, 10) obtained a crystalline substance, *raphanol* $C_{29}H_{53}O_4$, melting at 62° and soluble in ether, chloroform, benzene, or light petroleum.

According to Kellner (Landw. Versuchs. Stat. 1883, 30, 42), a gigantic variety of radish, single roots of which attain a weight of 2½ to 3 kilos., is much esteemed as a vegetable in Japan. He found this to contain—

Water	Protein	Fat	Soluble carbohydrates	Crude fibre	Ash
93·45	0·67	0·07	4·40	0·77	0·43

about two-thirds of the total nitrogen being present as real proteids. The ash contained—

K_2O	Na_2O	MgO	CaO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
46·4	2·4	4·7	9·4	0·6	10·1	13·1	2·6	11·9

The proportion of sulphur, in organic combination, in the roots, varies from 0·22 to 0·07 p.c.

Another Japanese species, *R. caudatus* (Linn.), is valued for its seed pods, which are about twice the size of those of the common radish, and are eaten as a salad or pickled in vinegar (Rep. New York Expt. Stat. 1884). According to Sacher (Chem. Zeit. 1910, 34, 1192 and 1333), the skins of the red radish, extracted for a few hours with their own weight of 90 p.c. alcohol, yield a solution which serves as a delicate and useful indicator for acids and alkalis, turning intensely red with the former and green with the latter.

H. I.

RADIUM. Symbol Ra. At.wt. 226. A radioactive element discovered by M. and Mme. Curie in the pitchblende from Joachimsthal (P. Curie, S. Curie and G. Bémont, Compt. rend. 1898, 127, 1215).

Occurrence. All ores containing uranium also contain radium. In the majority of them, the ratio of radium to uranium is equal to the 'equilibrium ratio' $3{\cdot}2\times10^{-7}$, *i.e.* 320 mgm. radium are present per ton of uranium (*v.* McCoy, Ber. 1904, 37, 2641). In *autunite*, a hydrated calcium uranium phosphate which occurs in France and Portugal, the proportion of radium is only from 20 to 80 p.c. of the above, radioactive equilibrium not having been established. Geologically, old formations contain a slightly larger radium ratio than the more recent formations (Mlle. Gleditsch, Le Radium, 1911, 8, 256).

The extremely delicate emanation test for radium reveals the presence of that element in all common rocks and minerals, and in natural springs, both hot and cold. Most of the celebrated spas contain appreciable quantities of radium or its emanation.

Radium preparations are usually prepared from pitchblende, an impure uranosouranic oxide, occurring in Cornwall, in Bohemia (Joachimsthal), &c.

Extraction from pitchblende. The crushed mineral, after a preliminary roasting in air, is heated with sodium carbonate in a reverberatory furnace. The product is washed with water and then with dilute sulphuric acid, to remove the uranium as soluble uranyl sulphate. All the radium is left in the insoluble residue, which consists mainly of lead and calcium sulphates, silica, alumina, and ferric oxide, but which contains small amounts of copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, rare earths, niobium, tantalum, arsenic, &c. The original method of working up these residues, due to Debierne, is as follows:

The residue is boiled with concentrated sodium hydroxide solution, to remove most of the lead sulphate, silica, and alumina, and the insoluble portion well washed. This is then attacked with hydrochloric acid, in which a large proportion dissolves. The radium is left in the insoluble portion, which is washed, again treated with sodium hydroxide, and the insoluble residue vigorously boiled with concentrated sodium carbonate solution to convert barium and radium sulphates into carbonates. The solid is filtered off, washed with sodium carbonate solution and then with water, and dissolved in hydrochloric acid. The filtered chloride solution is treated with sulphuric acid to precipitate radium and barium sulphates, which are contaminated with traces of lead and calcium sulphates. The sulphates are again converted into carbonates and then into chlorides. The acid chloride solution is treated with hydrogen sulphide, and the precipitate, which contains polonium, is removed. The filtrate is oxidised and treated with ammonia, when a precipitate is removed containing actinium. From the filtrate, radium and barium carbonates are thrown down, and the washed precipitate converted into chlorides. The solid chlorides are washed with concentrated hydrochloric acid to remove traces of calcium chloride, and the residual radium and barium chlorides are then separated by fractional crystallisation. This is effected at first from aqueous solution, but in the later stages, when the quantity of material containing radium has been largely reduced, solutions in hydrochloric acid of gradually increasing strength are used as solvent, since the solubility of the chlorides is thereby largely diminished. The final crystallisations are made from the most concentrated acid that can be prepared by distillation. Radium chloride, being less soluble than barium chloride, accumulates in the less soluble fractions (Mme. Curie, Translation of Thesis for Doctorate, Chem. News, 1903, 88, 85).

A similar method of treatment, employed on a large scale by Haitinger and Ulrich (Monatsh. 1908, 29, 485; *cf.* Paweck, Zeitsch. Elektrochem. 1908, 14, 619), has been more fully described. The residue is originally boiled with half its weight of sodium hydroxide (25 p.c. solution), the insoluble portion treated with one and a half times its weight of hydrochloric acid (1 : 1), and the solid residue boiled with half its weight of sodium carbonate (25 p.c. solution). This treatment with sodium carbonate is performed three times, to ensure the conversion of all the radium into carbonate. The subsequent treatment is essentially that already described.

One ton of Joachimsthal residues yields from 10 to 20 kilos. of the crude barium-radium sulphate mixture having an activity about sixty times that of uranium. A careful examination of the radium in all the by-products from the extraction of radium from 10 tons of Joachimsthal pitchblende, showed that there was present in all only 0·26 grm. of which two-thirds was present in the unattacked residue from the soda extractions, and about one-quarter in the lead products (H. Souczek, Sitzungsber. K. Akad. Wiss. Wien, 1910, 119, [ii.*a*] 371).

The radium-barium sulphate mixture may with advantage be reduced to sulphide by ignition in a current of coal gas, and then dissolved in hydrochloric acid (Soddy). The chlorides of radium and barium may be almost quantitatively precipitated from aqueous solution by saturating with hydrogen chloride.

The fractionation of the mixed *bromides* of radium and barium is said to be more rapid, but less regular, than that of the chlorides (Giesel, Ann. Chim. Phys. 1899, [ii.] 69, 91; Ber. 1902, 35, 3608). For another method of separating radium and barium *v.* Marckwald, Ber. 1904, 37, 88.

Preparation of radium. About 0·1 grm. of pure radium chloride was electrolysed in solution with a mercury cathode. The fluid radium amalgam was dried and carefully heated in an iron boat in a current of pure hydrogen under reduced pressure. At 400°, the amalgam became solid; no more mercury was evolved at 700°, and metallic radium was left in the boat (Mme. Curie and Debierne, Compt. rend. 1910, 151, 523). A metallic mirror, apparently containing radium, has been obtained by heating its azoimide $Ra(N_3)_2$ at 185°–250° in a vacuum (Ebler, Ber. 1910, 43, 2613).

Properties. Radium is a brilliant, white metal, which melts sharply at about 700° and volatilises appreciably at that temperature. It adheres strongly to iron. It tarnishes rapidly in the air, forming a nitride, and vigorously decomposes water with evolution of hydrogen, forming radium hydroxide solution.

Radium compounds closely resemble those of the alkaline earth metals, and particularly those of barium, with which they are isomorphous. The volatility of the bromides of calcium, strontium, barium, and radium diminishes in the order given (Stock and Heynemann, Ber. 1909, 42, 4088); but so far as the volatility of the elements is concerned, radium resembles calcium rather than barium. The physical and chemical properties of the compounds of the alkali and alkali earth metals usually show a well-marked graduation in the order calcium, lithium, strontium, barium, sodium, potassium, rubidium and cæsium, and in this scheme radium comes between barium and sodium (de Forcrand, Compt. rend. 1911, 152, 66).

The *chloride, bromide, nitrate, carbonate, sulphate, azoimide* and *platinocyanide* of radium are known. The salts are colourless when freshly prepared, but develop colour on standing; they are luminous in the dark, and continuously evolve heat at the rate of 118 calories per hour per grm. of radium (Schweidler and Hess, Monatsh. 1908, 29, 853; *cf.* Curie and Laborde, Compt. rend. 1903, 136, 673; Rutherford and Barnes, Phil. Mag. 1904, 7, 202).

The *chloride,* which is hygroscopic, closely resembles barium chloride; in preparing it in the pure state, care must be taken to eliminate the trace of lead chloride which is invariably present. Radium chloride is para-magnetic (Curie and Cheneveau, Soc. franç. de phys. 1903). The *bromide* is an unstable substance, losing bromine on keeping and passing into the hydroxide, and eventually, by absorption of carbon dioxide, into the carbonate (Giesel, *l.c.*; Ramsay, Monatsh. 1908, 29, 1013; Thorpe, *v. infra*). The freshly prepared anhydrous bromide has a beautiful blue fluorescence. The crystals of the bromide have been measured by Rinne (Centr. Bl. f. Min. u. Geol. 1903, 134). *Radium sulphate* is the least soluble sulphate known.

The ionic mobility of the radium ion is 57·4 (½Ra). For the electrochemical behaviour of radium, *v.* Coehn, Ber. 1904, 37, 811.

Spectrum. Radium salts colour the flame a pure carmine-red; the flame spectrum shows four bands in the red and one in the blue. The spark spectrum has been studied by Demarçay (Compt. rend. 1898, 127, 1218), Runge (Ann. Physik. 1903, 10, 407), Exner and Haschek (Wien. Ber. 1901, July 4), Runge and Precht (Ann. Physik. 1904, 14, 418), and Crookes (Proc. Roy. Soc. 1904, 72, 295). The most intense lines in the spark spectrum are 4683, 4436, 4341, 3814, 3650, 2814, 2709, and of those occurring in the photographic region of the spectrum, the strongest line is 3814, in the ultraviolet. The relative intensities of the two neighbouring lines, 4553·3 (radium) and 4554·2 (barium), furnishes a good test of the completeness of the separation of the two elements. The barium line is seen with the same intensity as the radium line when only 0·6 p.c. barium is present in a radium salt. A more stringent test (Huggins) is to compare the intensity of the line 5536·2 (Ba) with that of the lines 5813·8 and 5560·8 (Ra).

Atomic weight. The analogy between radium and the alkaline earth metals, and the isomorphism of radium and barium salts, shows that radium is a divalent metal, and its atomic weight is therefore twice its chemical equivalent. The first determinations, made on about 90 mgms. of radium chloride, gave the value 225 for the atomic weight (Mme. Curie, Ann. Chim. Phys. 1903, 30, 99), while later analyses of 0·4 grm. of the chloride, gave the value 226·2 as the mean of three concordant experiments (Mme. Curie, Compt. rend. 1907, 145, 422). This value was confirmed by Thorpe (Proc. Roy. Soc. 1908, 80 A, 298; Chem. News, 1908, 97, 229), who found the value 227 by the analysis of 60 to 80 mgms. of the chloride. Hönigschmid (Sitzungsber. K. Acad. Wiss. Wien, 1911, 120, [ii.*a*] 1), working with a gram of highly purified radium chloride, found for the ratio $RaCl_2$: 2AgCl the value 1·03554, whence Ra=225·95, and for the ratio $RaCl_2$: 2Ag, the value 1·37592, whence Ra=225·96. Gray and Ramsay (Proc. Roy. Soc., 1912, 86, A, 270) by converting the bromide into chloride and *vice versâ* have obtained the value Ra=226·36.

Runge and Precht calculated the value 257·8 for the atomic weight of radium, from spectroscopic considerations (Phil. Mag. 1903, [vi.] 5, 476); but according to Watts, their calculation, which involves an extrapolation, is only approximate, and when carried out more exactly, yields the value 226·6 (Watts, *ibid.* 1903, [vi.] 6, 64; 1909, [vi.] 18, 411), in good agreement with the chemical value.

Estimation of radium: chemically. The estimation of radium in a mixture of radium and barium salts can be effected by ordinary indirect analysis, *e.g.* determination of the weight of the mixed chlorides and the percentage of chlorine in the mixture. This method is only available when the radium forms an appreciable percentage of the mixture.

Physically. (i.) By measurement of its γ-radiation. A standard preparation of known radium content is required. The preparation to be examined must have been prepared at least a month, and preferably kept in a sealed tube, since the γ-radiation is due to the disintegration products formed from radium. A large lead electroscope is employed, provided with a single gold leaf insulated by a sulphur bead. The rate of leak is determined for a weight w_1 of the material under examination and a weight w_2 of standard substance. Call these rates r_1 and r_2 scale divisions per minute respectively. The calculation may be illustrated with reference to the examination of a pitchblende for radium, supposing that the standard employed was a pitchblende containing p p.c. of uranium. The percentage x of uranium in the substance is given by

$$x=\frac{w_2}{w_1}\times\frac{r_1}{r_2}\times p=q \text{ say,}$$

and from the 'equilibrium ratio' (*v.* p. 544) the amount of radium is given by $0{\cdot}01q\times0{\cdot}32 = 0{\cdot}0032q$ grms. radium per ton of material.

From 20 to 100 grms. of a pitchblende should be taken, according to its richness; larger quantities of other substances, poorer in radium, must be used.

In the presence of thorium, this method gives results too high, owing to the penetrating γ-radiation of mesothorium being measured as well. This may be allowed for in the case of a preparation that can be dissolved and the solution evaporated to dryness, for the radium emanation escapes, and three hours afterwards the γ-activity is that due to the mesothorium alone.

(ii.) The Emanation method. Solutions containing from 10^{-8} to 10^{-10} grms. of radium may be acidified, sealed up in a small distilling flask and the radium emanation allowed to accumulate for a month, when the equilibrium amount is present. The emanation is then boiled out of the solution in a slow stream of air, and the air dried and passed into an exhausted electroscope. The leak, 3 hours after admission, is measured. Comparison with a standard substance in a similar flask is necessary (Lloyd, J. Phys. Chem. 1910, 14, 476; Mme. Curie, Le Radium, 1910, 7, 65; *cf.* also *ibid.* 1909, 6, 195).

For the radioactive properties of radium and its compounds, *v.* RADIOACTIVITY.

RAFFINOSE, MELITOSE, *v.* CARBOHYDRATES.

RAMALIC ACID. Ramalic acid (lecanoric acid monomethyl ether) $C_{17}H_{16}O_7$ was isolated from the lichen *Ramalina pollinaria* (Hesse, J. pr. Chem. [i.] 57, 253) by means of ether. It crystallises in colourless needles, m.p. 179°–180°, and gives with alcoholic ferric chloride a violet colouration. It differs from the isomeric evernic acid which occurs in conjunction with it, by its sparing solubility in ether (Zopf, Annalen, 297, 306), but when hydrolysed with baryta water behaves similarly with the production of orcin, carbon dioxide, and everninic acid (compare article on EVERNIC ACID).

A. G. P.

RAMIE *v.* CHINA GRASS.

RAPE, *Brassica Napus oleifera* (DC.). Winter rape, a plant grown largely for the sake of its seeds which are rich in oil (*v.* RAPE OIL); also to some extent as forage for sheep and as a catch crop. Summer rape, or colza, is another variety, *Brassica Napus annua* (Koch).

According to König, the seeds contain, on the average—

Water	Protein	Fat	N-free extract	Fibre	Ash
7·3	19·6	42·2	20·8	6·0	4·2

The seeds, and indeed the whole plant, contains a pungent volatile oil—a mustard oil—which is not identical with allyl thiocarbimide and is less poisonous than that substance (Sjollema, Landw. Versuchs. Stat. 1900, 54, 311). It is, however, hurtful to animals, and the use of rape cake—left after expression of the oil from the seeds—as a food for cattle not infrequently causes death (Jörgensen, Bied. Zentr. 1898, 27, 697). According to Jörgensen (Landw. Versuchs. Stat. 1899, 52, 269; *ibid.* 1910, 72, 1), the thiosinamine from rape cake always contains less nitrogen than corresponds with the allyl compound (24·14 p.c.), and the higher the percentage of nitrogen in the thiosinamine from the cake, the more pungent is the odour and the more poisonous the cake. He concludes that if a cake yields, on treatment for an hour with white mustard (to supply the enzyme, emulsin), more than 0·5–0·6 p.c. of mustard oil, and if the thiosinamine obtained from the mustard oil contains more than 22 p.c. of nitrogen, there is danger of the cake being poisonous to cattle. Moreover, the pungent taste of the cake renders it unpalatable, and in England it is seldom used as a food, but is employed as a manure, chiefly for the sake of the nitrogen (about 5–6 p.c.) which it contains. It is a slow acting manure.

Green rape, before or during flowering, forms a useful food for sheep. According to Kellner winter rape, in flower, contains—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
85·9	2·8	0·8	5·7	3·5	1·3

Of the total protein, 1·3 p.c. is digestible proteids. It is occasionally made into hay, which, according to Kellner, has the composition—

Water	Protein	Fat	N-free extract	Crude fibre	Ash
15·5	15·7	4·4	34·6	20·5	9·4

Of the protein, 8·5 p.c. is digestible proteids.

H. I.

RAPE OIL (COLZA OIL). The various kinds of rape oil are obtained from the seeds of *Brassica campestris* and of several largely cultivated varieties of this species, belonging to the natural order *Cruciferæ*. The oils from these plants are, especially in this country, indiscriminately termed rape oil or colza oil; on the Continent, however, two different kinds of oil are understood under the last two names. According to the variety of the plant from which the seed is derived, the following oils may be broadly differentiated:—

1. Rape oil (*Huile de navette; Rapsoel, Repsoel*), from the seeds of *Brassica Napus* (Linn.).

2. Rübsen oil (*Huile de rabette; Rueboel, Ruebsenoel*), from the seeds of *Brassica campestris* (*B. Rapa*, Linn.).

Both Brassica species furnish several, by no means sharply distinguished, varieties, which are again divided, according to the season of the year, into several forms (*see* Lewkowitsch, vol. ii. 198).

Rape seed is grown in almost all European countries. In France and in Belgium the winter variety of *Brassica Napus* is chiefly cultivated. Enormous quantities are grown in East India. The bulk of the East Indian seed is imported into England from Calcutta, Madras, Bombay (Guzerat and Ferozepore).

Rape seed is crushed between rollers, and the meal is either expressed or extracted with carbon disulphide or petroleum ether. The extracted oil is, as a rule, purer than the expressed oil, since a considerable amount of mucilaginous matter passes into the oil when the seed is expressed. The cakes obtained by expression form an excellent cattle food, if the seed has been tolerably pure, *i.e.* free from mustard seeds and wild seeds. The extracted meal is unsuitable as cattle food, and is chiefly used as manure, at any rate in this country, although some meal, especially on the Continent, finds its way into compound cakes.

Rape (colza) seed contains from 33 to 43 p.c. of oil. The seed harvested in the north of France contains 43–45 p.c.; Danubian seed 38–40, and Indian seed from 42 to 45 p.c.

The crude oil is dark in colour, and before being put on the market, it is refined by treatment at the ordinary temperature with about 1 p.c. of strong sulphuric acid (Thenard's process), which coagulates and carries down the impurities. The settled oil is then washed with water until free from mineral acid.

The refined oil of commerce is pale yellow; it possesses a characteristic smell (which may serve to identify the oil) and, except for the finest qualities, an unpleasant harsh taste. The term 'colza oil' can no longer be taken as referring to the special oil expressed from the finest French seed as was the case about forty years ago. For as the consumption of colza oil extended, the seeds from other countries were used for the manufacture of 'colza oil,' especially German seed, such as Rübsen seed from *Brassica campestris* (*B. Rapa*). Since Indian rape seed is being refined in large quantities, the term 'colza oil' has become a generic term, denoting a fine rape oil from various kinds of rape seed. Therefore the restriction of 'colza oil' to a French oil or even a German oil no longer holds good, and 'colza' oils are sold in trade which are made from Indian seed, such as Cawnpore seed and Guzerat seed. It should be noted that 'colza oil' was originally an oil which had been obtained by expression, and the term 'best refined colza oil' must still be held as rightly belonging to an expressed oil, such as is used for edible purposes. This class of edible rape oil is largely used by bakers for greasing the ends of loaves in the oven ('bread oil').

There are also in commerce pure refined colza oils which have been obtained by extraction with solvents. These are of distinctly inferior quality, and their taste reveals their origin immediately. Colza oils of this class are not objectionable as burning oils, but being, as stated already, of a distinctly inferior quality, they are valued in the trade at a lower figure.

Jamba oils approximate to rape oils as regards quality; as these jamba oils are now coming in larger quantities on the market, the distinction between rape oils and jamba oils has gained some importance.

Glycerides of the saturated fatty acids occur in rape oil to a small amount only. Amongst the unsaturated fatty acids erucic and rapic acids have been identified. Owing to the high molecular weight of erucic acid, the saponification value of rape oil is lower than in the majority of fatty acids (*see* Oils, Fixed, and Fats). For the chemical and physical characteristics *see* tables under Oils, Fixed, and Fats.

The 'cold drawn' oil is used as an edible oil, especially in India. It is also used as an edible oil on the Continent, and in this country as 'bread oil.' The various qualities of refined oil have been mentioned above. Those colza oils, which are unsuitable for edible purposes, find an outlet as excellent burning oils. Equally well-refined oils can also be used as 'wool oils.' Enormous quantities of the oil are used for lubricating purposes, both in the refined state and as 'blown rape' oil. Smaller quantities are used on the Continent for the making of soft soap. Rape oil is further largely used for quenching steel plates. J. L.

RAPHIA WAX *v.* Waxes.

RASPBERRY, *Rubus Idaeus* (Linn.). According to König, the fruit contains—

Water	Protein	Free acid, malic	Invert sugar	Cane sugar	Other N-free extract	Fibre and seeds	Ash
85·0	1·4	1·5	3·4	0·9	1·0	6·4	0·5

The odour and flavour of raspberries are apparently due to an essential oil, which has a sp.gr. of 0·8863, at 15° saponification value 193, is dextro-rotatory and soluble in 30 parts of 80 p.c. alcohol (Haensel's Report, Oct. 1904).

The free acid in the juice contains tartaric (0·18 p.c.), citric (0·65 p.c.), malic (0·30 p.c.), and volatile acids (equivalent to 0·04 p.c. of acetic acid) (Kayser, Zeitsch. öffentl. Chem. 1906, 12, 155). Windisch (Zeitsch. Nahr. Genussm. 1903, 6, 447) and Utz (Chem. Zentr. 1903, ii. 841) have found salicylic acid in pure raspberry juice. The amount obtained was about 1·1 mgrm. per litre of juice, and it is believed to exist as an ester in the fruit. According to Röhrig (Zeitsch. Nahr. Genussm. 1910, 19, 1) formic acid to the extent of 0·000176 p.c. occurs in fresh raspberries. According to Hefelmann, Mauz, and Müller (Zeitsch. öffentl. Chem. 1906, 12, 141), fresh raspberry juice contains on the average 4·09 p.c. of total solids and 0·43 p.c. of ash.

The seeds of raspberries contain 14·6 p.c. of a drying oil of sp.gr. 0·9317, at 15° saponification number 192·3, iodine number 174·8. The liquid fatty acids consisted chiefly of linolic and linolenic acids, with small quantities of oleic and *iso*-linolenic acids (Kržižan, Zeitsch. öffentl. Chem. 1907, 13, 263).

Raspberry syrup is made by boiling about 35 parts of raspberry juice with 65 parts of cane sugar. According to Spaeth (Zeitsch. Nahr. Genussm. 1901, 4, 97, 920), in genuine raspberry syrup the amount of ash from 100 grms. should not be below 0·2 grm., and this should require for neutralisation at least 2·0 c.c. of normal acid. The acidity of 100 grms. of the syrup should correspond to from 7 to 13 c.c. normal caustic potash. H. I.

RAURACIENNE *v.* Azo- colouring matters.

RAVISON OIL. The oil from Black Sea rape seed, a kind of wild *Brassica campestris*, is termed in commerce Black Sea rape oil or ravison oil. The seed contains 33–40 p.c. of oil.

Ravison oil has a higher iodine value than rape oil, and exhibits stronger drying properties. It is therefore not so suitable for lubricating purposes as the latter, and its admixture with, or substitution for, rape oil must be looked upon as adulteration. Since ravison oil is mostly extracted by means of solvents, traces of the latter are left in the oil. They are most readily detected by taking the flash point of the oil. For the characteristics of the oil, *see* tables under Oils, Fixed, and Fats.

J. L.

REALGAR (*Sanaracha* of the ancients). Native arsenic monosulphide, AsS, crystallising in the monoclinic system. Crystals are not infrequent; these are transparent with a bright aurora-red colour and a brilliant lustre; but on exposure to light they very soon crumble down to a yellow powder consisting of a mixture of arsenic trioxide and arsenic trisulphide. Realgar is found, associated with orpiment (*q.v.*), in mineral-veins at several places in Hungary, and at Allchar in Macedonia; and in beds of sandy clay at Mercur in Utah. Mixed with saltpetre, it gives the 'white fire' of pyrotechnic displays. It has also been used in calico-printing, in tanning for removing the hair from skins, and in the manufacture of shot. The material now used is prepared artificially from the white arsenic derived from mispickel. L. J. S.

REAUMUR'S PORCELAIN. Glass in the process of working will often acquire a peculiar opacity. This appears to depend on a physical change, since by a carefully-constructed process a kind of crystallisation may be set up, producing the porcellaneous appearance. Reaumur attempted to introduce a material of this description in the place of pottery (Ure).

RECTIFICATION is the term applied to the second and subsequent distillations of a volatile liquid to free it from the impurities which may have passed over in the first distillation. More particularly applied to the distillation of alcohol (*q.v.*): *v.* also Distillation.

RED, ANISOLE, *v.* Azo- colouring matters.

RED ANTIMONY. *Antimony oxysulphide* or *kermesite v.* Antimony.

RED, ARCHIL, *v.* Azo- colouring matters.

RED CHALK. An earthy or argillaceous iron ore, used as a drawing or marking material; also in geology for beds of chalk of a brick-red colour (a calcareous rock coloured by ferric oxide) (v. Reddle).

RED, CHROME. *Basic lead chromate v.* Chromium.

RED, CLARET, *v.* Azo- colouring matters.

RED CLOVER FLOWERS, *Trifolium pratense* (Linn.), which have a limited application in medicine as an alterative, and in the treatment of cancer, have been examined by Power and Salway (Chem. Soc. Trans. 1910, 97, 231), and found to yield 0·028 p.c. of essential oil, containing furfuraldehyde of sp. gr. 0·9476 at 20°/20°; $\alpha_D + 4° \, 0'$ in a 1 dcm tube; a large amount of sugar giving *d*-phenyl glucosazone (m.p. 205°); salicylic and *p*-coumaric acids; *iso*-rhamnetin $C_{16}H_{12}O_7$ (m.p. 295°), probably present as a glucoside; and a number of phenolic substances, among them—*pratol,* a hydroxymethoxy flavone, $C_{15}H_8O_2(OH)(OCH_3)$; *pratensol* $C_{17}H_9O_2(OH)_3$ (m.p. 210°); and the following glucosides: *trifolin* $C_{22}H_{22}O_{11}H_2O$ (m.p. 260°), which yields on hydrolysis *trifolitin* $C_{16}H_{10}O_6$ (m.p. 275°), and rhamnose; *iso-trifolin* $C_{22}H_{22}O_{11}$ (m.p. 250°), and a glucoside of quercetin (m.p. 235°). From the resin in the dried flowers, which was present to the extent of 5·6 p.c., were obtained *myricyl alcohol, heptacosane, pentricontane; sitosterol;* a dihydric alcohol, *trifolianol* $C_{21}H_{34}O_2(OH)_2$ (m.p. 295°); and a mixture of fatty acids, consisting chiefly of palmitic, stearic, and linolic acids, with small amounts of oleic, linolenic, and *iso*-linolenic acids.

RED, CONGO, *v.* AZO- COLOURING MATTERS.

RED COPPER ORE *v.* CUPRITE.

RED CURRANT, *Ribes rubrum* (Linn.). The fruit is used for table purposes. According to König, the average composition of the ripe fruit is—

Water	Protein	Free acid, malic	Invert sugar	Cane sugar	Other N-free extract	Fibre and seeds	Ash
84·3	0·5	2·2	6·4	0·1	1·2	4·6	0·7

According to Guignard (Compt. rend. 1905, 141, 448), the leaves of red currant contain a substance which yields hydrocyanic acid in small quantities, the largest amount, in June, being about 0·0025 p.c. of hydrogen cyanide; the twigs contain very little and the roots none. For a study of the fermentation of red currant juice and analyses of the resulting wine, *see* Keim (Zeitsch. anal. Chem. 1891, 30, 401).

H. I.

RED, DIAMINE, *v.* AZO- COLOURING MATTERS.

RED DURA. The 'Red Dura' or 'Durra' of the Soudan, also known as 'Shikytan,' consists of the deep reddish-brown sheaths of a grass, apparently the *Andropogon Sorghum* (Brot.) var. *vulgaris,* also known as the *Sorghum vulgare* (Pers.) or 'Great millet,' the grain of which provides so important a foodstuff. According to E. P. Browne, Inspector of the Blue Nile Province, the 'shikytan' is used for producing a red dye, practically utilised for staining a grass called 'lanzura,' employed in the manufacture of coloured 'bursh' mats, but occasionally for the leather of 'markubs' (Sudanese shoes). It is specially grown for dyeing purposes. A full account of the *S. vulgare* is given by Watt (Dictionary Economic Products of India, 6, iii. 289). The grain occasionally possesses a brick-red colour, and that at Harihar is used for preparing a red morocco from goat skin. The canes of *S. saccharatum* also, when pressed and allowed to ferment, develop a red or reddish-brown colour, and the dye thus produced can be extracted by means of dilute alkali. The Indian, Persian, Abyssinian, and Egyptian forms would seem to be derived from the *A. Sorghum,* var. *durrha;* but the fact that this plant is so extensively cultivated in Egypt as a foodstuff and the 'Shikytan' is grown entirely for dyeing purposes, seems to indicate that this latter is again a special variety.

The colouring matter, *durasantalin,* to which the formula $C_{16}H_{12}O_5$ has been provisionally assigned (Perkin, Chem. Soc. Trans. 1910, 97, 220), consists of a bright-red or scarlet powder, possessing an ill-defined crystalline structure. It is soluble in alkalis with a red-violet colour, passing rapidly to brown on air oxidation, gives with alcoholic ferric chloride a brown liquid, and when fused with alkali, p-*hydroxybenzoic acid* and *phloroglucinol,* together with a trace of a third substance, probably p-*hydroxyacetophenone* are produced. Durasantalin does not dye mordanted calico, but behaves as a substantive dyestuff towards wool upon which it produces a dull-red shade. A very permanent and slightly fuller colour can be produced by previously mordanting the wool with chromium. In many respects this dye resembles the santalin of sanderswood, but there is no doubt that these substances are chemically distinct.

A. G. P.

RED, FAST, *v.* AZO- COLOURING MATTERS.

RED FIRE *v.* STRONTIUM.

RED HÆMATITE or red iron-ore, *v.* HÆMATITE.

RED, HESSIAN, *v.* AZO- COLOURING MATTERS.

RED LEAD. *Minium* Pb_3O_4 *v.* LEAD.

RED LIQUOR. *Crude aluminium acetate v.* ACETIC ACID; also WOOD, DESTRUCTIVE DISTILLATION OF.

RED MANGANESE. Known also as *dialogite, v.* RHODOCHROSITE and RHODONITE.

RED, NAPHTHAMINE, *v.* AZO- COLOURING MATTERS.

RED OCHRE. Oxide of iron mixed with argillaceous matter.

RED OIL *v.* OLEIC ACID.

RED ORPIMENT. *Realgar* q. v.

RED PRECIPITATE. *Mercuric oxide,* HgO *v.* MERCURY.

RED SHORT. Iron and other metals which are brittle at a red heat are said to be red short.

RED SILVER ORE *v.* PROUSTITE and PYRARGYRITE; also SILVER.

RED, VENETIAN, *v.* PIGMENTS.

RED WOOD *v.* BRAZILWOOD.

REDDLE or **RUDDLE** is a soft, red, iron ore, more or less impure, commonly associated with deposits of hæmatite, as in the Forest of Dean, at Ulverston, and at Whitehaven. It may be regarded as a kind of red ochre, mixed with argillaceous matter, and is used chiefly for marking sheep.

REDONDA PHOSPHATE *v.* under art. ALUMS; also FERTILISERS and PHOSPHORUS.

REDRUTHITE. A variety of cuprous sulphide, known as *chalcosine, copper glance,* or *vitreous copper* found in Cornwall, particularly in the neighbourhood of St. Just, in various parts of Scotland, and both crystallised and massive in the porphyritic district in Ulster, and at the Kenmare mines, Kerry. *V.* COPPER GLANCE.

REDUCTASES *v.* FERMENTATION.

REDUCTION. The abstraction of an electronegative element from, or addition of an electropositive element to, any compound; thus an oxide, deoxidised by the action of hydrogen, charcoal, &c., is said to be reduced. The addition of hydrogen to an organic compound by the action of sodium amalgam, &c., is also called an operation of reduction.

REFRACTOMETER. In the chemical examination of liquids and solutions a knowledge of the refractive index is often very valuable. Such a method of characterisation, however, could not become of any very general practical utility so long as a spectrometer and a hollow prism were necessary in the determination of refractive power. A rapid measurement of the refractive index of a liquid with a small quantity of material has become possible only by the introduction of instruments based on the principle of total reflection.

If A is a point in the common surface of two media, the upper of which is air, and the lower some pure liquid, then the ray of light BA, on entering the denser medium, is refracted nearer the normal GAF in the direction AC, so that $\frac{\sin i}{\sin r}=n$, where n is the refractive index of the liquid. The ray DA, entering the liquid at A under grazing incidence will be refracted according to the same law, and we have accordingly $\frac{\sin 90°}{\sin R}=n$. Obviously, R is a limiting or critical angle, and it is impossible to illumine the shaded part of the denser medium by any rays entering at A; AE is therefore a boundary between light and dark. Conversely, if A is illumined from the side of the denser medium, these rays which proceed from points in the shaded area cannot pass out into the air, but are totally reflected. Further, it is clear from the relationship $\frac{\sin 90°}{\sin R}=n$ that if we can determine the critical angle R, the index of refraction of the lower medium is easily evaluated. Instruments the object of which is the measurement of the critical angle are known as 'refractometers,' and an actual observation with one of these consists in the determination of the position of a boundary between light and dark, such as that referred to above.

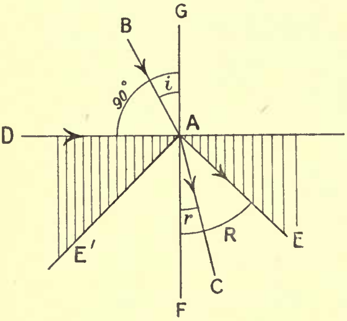


FIG. 1.

The instruments chiefly used either for purely scientific or technical chemical work are (1) Pulfrich's refractometer, (2) Abbe's refractometer, (3) the butter refractometer, (4) the dipping refractometer.

Pulfrich's refractometer.—The essential part of this instrument is a rectangular glass prism (*see* Fig. 2), so mounted that of the surfaces which are at right angles to each other, one (AB) is horizontal, and the other (CD) is vertical. On the top of the prism there is cemented a small glass vessel, which holds the liquid under investigation. It is essential that the index of refraction of this liquid should be less than that of the prism. The horizontal surface AB is illumined by monochromatic light entering the liquid from the left. If the ray which passes from the liquid into the prism under grazing incidence is considered, its path will be as shown in Fig. 2, and will be marked by a boundary between light and dark. The position of this limiting ray, after it has passed out of the prism into the air, is known when the angle i which it makes with the horizontal is determined. This is effected with the aid of a telescope fitted to a moving circular scale, the crosswires of the telescope being adjusted to the boundary between light and dark.

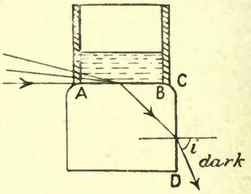


FIG. 2.

It can easily be shown that, if n is the index of refraction of the liquid under investigation and N is the index of refraction of the glass prism, $n=\sqrt{N^2-\sin^2 i}$. The value of N having been determined once for all, the index of refraction of the liquid can be easily deduced from the observed value of i. In actual practice tables are supplied with each instrument, in which, for a given prism at a given temperature and for sodium light, the corresponding values of i and n are recorded.

In view of the variation of refractive power with change of temperature, it is essential to keep both liquid and prism at a definite constant temperature. This is done by passing a current of tempered water through the mount in which the prism is set and also through a silver vessel which can be lowered into the glass cell containing the liquid. Reference will be made later to the methods of securing a water current of steady temperature.

Fig. 3 shows the general appearance of Pulfrich's refractometer. The mount in which the prism is set is seen at L, surmounted by the short glass cylinder which holds the liquid. S, the silver vessel through which the water current circulates, is raised or lowered by means of a screw, and can be moved to one side on the axis M. The telescope EF is fitted rigidly to the divided circle D, which is free to rotate except when clamped by the screw just seen at H. The final adjustment of the cross-wires to the boundary between light and dark is made by means of the micrometer screw G. Connected with this screw there is a graduated drum-head moving in front of a horizontal scale, so that it is possible to determine accurately the dispersion for any given liquid.

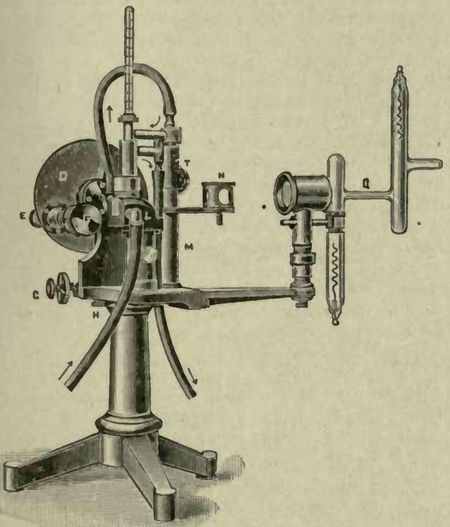


Fig. 3.

As source of light, either a coloured flame or a Geissler tube (as at Q) may be employed. In the former case the burner is set up on one side and the image of the flame is thrown into the liquid by means of the prism N. This prism is movable about M as an axis, and can be displaced when it is desired to use the Geissler tube.

The Pulfrich refractometer, although chiefly used for investigations of a purely scientific nature, has been employed in the estimation of alcohol and extract in beer and wine (see Riegler, Zeitsch. anal. Chem. 1896, 35, 27; Race, J. Soc. Chem. Ind. 1908, 27, 544, 547). The accuracy of the instrument is 1 unit in the fourth decimal place in measurements of refraction, and 1–2 units in the fifth place in measurements of dispersion. Although designed mainly for the determination of the refraction and dispersion of liquids, Pulfrich's refractometer can be employed also in the optical investigation of solid bodies. In this case the small glass cylinder is removed, and the polished object is placed on the top of the prism of the apparatus. Contact between the two solids is secured by introducing a drop of a liquid with a refractive index greater than that of the body under investigation. For the majority of glasses monobromonaphthalene is a suitable liquid to use in this way.

Attention may be drawn (*see* Lewkowitsch, J. Soc, Chem. Ind. 1909, 28, 773) to another refractometer which bears a general resemblance to the Pulfrich instrument, but differs from it in that the rectangular prism of the latter is replaced by a cylinder quadrant. This refractometer can be used in determining the refractive power of solid, liquid, or gaseous substances, and it is claimed that the dividing line between light and dark is more sharply defined than in the Pulfrich instrument.

The Abbe Refractometer. The essential feature of this apparatus, primarily designed for the investigation of fluids, is a double prism which can be rotated about a horizontal axis. The double prism consists of two similar prisms of highly refracting glass placed face to face and mounted in hollow metal cases. The lower prism with its case is removable, but usually hinges at one edge with the other case, and is kept in position by a clamp. When an observation is to be made the double prism is opened out, and a few drops of the liquid under investigation are placed on the ground surface of the lower prism. The prism faces are then brought together, the apparatus being inclined at an angle so that the liquid does not run off, and the clamp is fixed. A thin film of the liquid is thus enclosed between the two prisms. White light is thrown into the lower prism by means of a plane mirror mounted on the base of the instrument, and each point, therefore, on the ground surface of this prism becomes a centre of radiation. Each point, then, on the polished face of the upper prism will be illumined by rays coming from all directions through the liquid. Provided that the index of refraction of the upper prism is greater than that of the liquid, and supposing for the moment that monochromatic light is being employed, the rays converging on any selected point A (*see* Fig. 4) will all pass into the upper prism, but the one which enters at grazing incidence will give a limiting ray AB in the upper prism, corresponding to a boundary between light and dark, so far as illumination at A alone is considered. Similarly, from any other selected point A′ there will pass through the prism a limiting ray A′B′, parallel to AB. When they emerge from the prism, all these limiting rays will still be parallel, as BC, B′C′, &c.

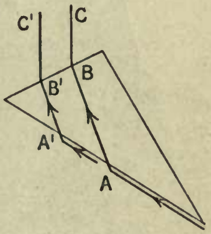


Fig. 4.

The telescope of the Abbe refractometer, F in Fig. 5, contains a lens which focusses these parallel limiting rays at the point in the telescope where the crosswires are placed. If it is borne in mind that the prisms have a definite width, it is clear that in the field of the telescope all the limiting rays will be focussed to a line, which will be a boundary between light and dark. In using the Abbe refractometer the double prism is rotated by the arm J until this boundary passes through the intersection of the crosswires of the telescope. The angle of adjustment of the arm is quantitatively related to the refractive index of the liquid, and might be used to compute the latter. In the Abbe instrument, however, the index of refraction of the liquid is read off directly on a graduated sector, S, which is rigidly connected with the telescope.

When, as is usual, this refractometer is used with ordinary white light, the boundary between the light and dark halves of the field is coloured, and no exact adjustment is possible. To obviate this difficulty a compensator is introduced in the telescope between the objective and the double prism. This compensator consists of two Amici prisms which can be simultaneously rotated in opposite directions about the axis of the telescope by means of the screwhead M, and so neutralise the dispersion of the border-line. A reading of the scale of the drum of the compensator permits a computation of the mean dispersion for the liquid under investigation.

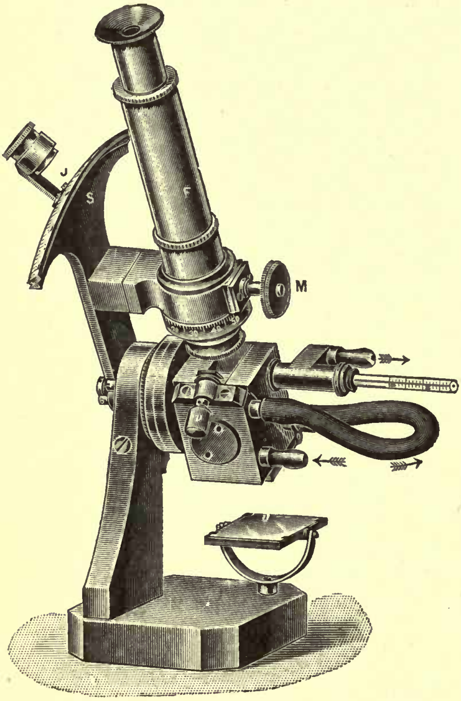


FIG. 5.

The accuracy of the Abbe refractometer is about 2 units in the fourth decimal place of the refractive index. In view of the variation of the refractive power of liquids with temperature, it is essential in accurate work to keep the prisms and the liquid at a definite constant temperature. Provision is made in the Abbe instrument for circulating water of constant temperature through the double-walled metal cases in which the prisms are mounted.

The Abbe refractometer has been employed in the examination of edible fats and oils, lubricants, alkalis, linseed oil, varnish, turpentine, petroleum, paraffin, beeswax, glycerol, aniline, aqueous, alcoholic, and ethereal solutions, milk serum, jams, jellies, and confectionery. So far as the examination of the majority of fats and oils is concerned, the Abbe instrument has to a large extent been displaced by the butter refractometer described below. The range of the former, however, is much wider than that of the butter refractometer, and the Abbe instrument is necessary for use with the highly refracting essential oils. Further, it stands a high temperature better than the butter refractometer, and is therefore particularly well adapted for the examination of substances with a high melting-point, such as beeswax and paraffin.

Butter Refractometer. The main parts of this instrument are a telescope and a double prism. As in the Abbe refractometer, the two prisms are mounted in metal cases with double walls, in order to permit the circulation of a current of water of constant temperature. The upper prism, however, is rigidly connected with the telescope, while a further difference from the Abbe instrument consists in the absence of a compensator in the telescope. The upper prism is specially constructed so that the border line of total reflection is achromatised for pure butter when white light is used for illumination. The telescope objective is adjustable in a slide by means of a micrometer screw (seen at C in Fig. 6), and in the focal plane of the objective there is placed an arbitrary scale, graduated from −5 to +105, the scope of which covers the interval from $n_{\text{D}}=1{\cdot}42$ to $n_{\text{D}}=1{\cdot}49$. The position of the border line of total reflection can, with the help of the micrometer screw, be determined to within one-tenth of a scale division, corresponding with an accuracy of 1 unit in the fourth decimal place of the refractive index. Each instrument is accompanied by a table, which gives scale divisions in terms of refractive indices, and *vice versâ.*

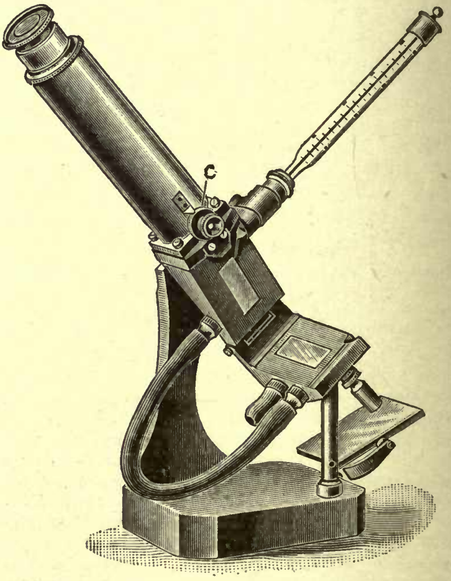


FIG. 6.

When a fat or oil other than butter is enclosed between the prisms, the border-line of total reflection is more or less coloured. The fringe is blue when the dispersive power is higher, and red when the dispersive power is lower, than that of butter fat. In the examination, therefore, of a sample of butter for adulteration it is desirable to note, not only the exact position of the borderline, but also its appearance. The band of colour seen at the border line with fats and oils other than butter fat is in the majority of cases not broad enough to interfere with a satisfactory reading. Should an exact reading be impossible, it is advisable to use a sodium burner as the source of illumination.

In the following table there are recorded the scale readings observed for various fats and oils in the butter refractometer at standard temperatures :—

Fats at 40°		Oils at 25°	
Butter	40·5–44·4	Cottonseed oil	67·6–69·4
Margarine	50·3–58·2	Linseed oil	87·5
Oleomargarine	48·6–49·2	Almond oil	64·0–64·8
Beef tallow	49·0	Poppyseed oil	72·0–74·5
Lard	50·0–51·2	Olive oil	62·0–62·8
Goose fat	50·0–50·5	Colza oil	68·0
Mutton tallow	45·0–46·0	Sesamé oil	67-0–69·0
Cocoanut oil	33·5–35·5	Cod liver oil	75·0
Cacao butter	46·0–46·5		

The position of the border-line for a given fat or oil varies with temperature, the mean variation amounting to 0·55 scale division per degree centigrade. The scale reading becomes lower as the temperature rises. For the conversion of a reading taken at any temperature into the equivalent value at the standard temperature various rapid methods have been suggested (*see* Leach and Lythgoe, J. Amer. Chem. Soc. 1904, 26, 1193; Richmond, Analyst, 1907, 32, 44). In this connection mention may be made also of Wollny's device of using the thermometer itself as an indicator of the highest scale values admissible in the case of pure butter at various temperatures between 30° and 40°.

Although primarily designed for the examination of butter and allied fats, the butter refractometer has been utilised also in testing such products as varnish, turpentine, petroleum, and glycerol.

Another instrument which closely resembles the butter refractometer is the milk-fat refractometer. This apparatus is designed for the determination of fat in milk, and the scale covers the interval from n_D=1·33 to n_D=1·42. The milk is curdled, the fat is extracted with a definite quantity of ether, and the refractive power of the ethereal solution is determined in the refractometer. The construction and manipulation of this instrument are the same as in the case of the butter refractometer.

Dipping Refractometer. A considerable extension of refractometric methods in chemical work has resulted from the introduction of this instrument. It is especially suited for the examination of dilute aqueous solutions, of which fair quantities (20–30 cc.) are available. The characteristic part of the dipping refractometer is the prism, which projects from the lower end of the instrument and is immersed directly in the liquid under examination. The body of the prism is cylindrical in shape, and it is so mounted that nothing but glass comes in contact with the liquid. By means of a mirror white light is thrown into the beaker containing the liquid in such a way that the rays enter the prism at grazing incidence, and give rise to a boundary between light and dark in the manner already described. The various parallel limiting rays are focussed by the objective to a line at the position in the telescope where the scale is placed. This border-line would, in ordinary circumstances, be fringed with colour, owing to the difference in dispersion between glass and liquid. The instrument is therefore provided with a compensator, similar to that already described in connection with the Abbe refractometer. This compensator, situated between the prism and the objective, consists of two Amici prisms, which can be rotated about the axis of the telescope by means of a milled ring.

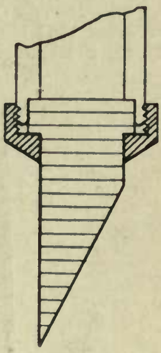


FIG. 7.

The border-line is much sharper in the dipping refractometer than in those instruments in which the liquid is enclosed between two prisms. On this ground a higher magnification in the telescope is permissible, and the accuracy of the measurement is correspondingly increased. The scale in the dipping refractometer is graduated from −5 to +105, and covers the range of refractive index from n_D=1·32539 to n_D=1·36640. With the help of a micrometer screw, which effects the sliding of the scale relatively to the border-line, it is possible to ascertain the position of the border line to one tenth of a scale division, so that the accuracy of the measurement is about four units in the fifth decimal place of the refractive index.

In working with the dipping refractometer a strict control of the temperature is necessary. This is best effected by immersing the beakers which contain the liquids under examination in a bath kept at a constant standard temperature. Care must be taken that the prism of the refractometer and the liquids in the beakers have reached the temperature of the bath before a measurement is made. It is convenient, when large numbers of solutions are to be examined, to have a metal frame in the bath so that the various beakers may be placed in a row and the refractometer slid along from one to another on a wire frame to which it is hooked (Fig. 8). If a circular bath is used, the beakers may be arranged in a circular frame, which is moved round so as to bring each beaker in succession under the refractometer. The standard temperature usually employed is 17·5°, at which temperature distilled water gives a scale reading of 15·0.

By various devices the dipping refractometer may be adapted to the examination of certain special cases. A volatile liquid, an ethereal solution for instance, may be enclosed in a metal vessel with a glass bottom; this fits the end of the refractometer air- and water-tight. The metal vessel is then immersed in the constant temperature bath, and the measurement is made in the usual way. If only a very small quantity of liquid is available, as in the case of blood serum, or if the liquid is deeply coloured, as in the case of dark beers, use may be made of an auxiliary prism. A few drops of the liquid are applied to the hypotenuse face of this prism, which is then slid along the polished elliptical face of the refractometer prism, and is kept in position by the metal vessel already mentioned.

The dipping refractometer has been used in the examination of a large variety of solutions. Provided that there is only one dissolved substance, the refractometer may be employed to determine the strength of the solution, and in this respect it is an instrument of great precision; it permits, for instance, the detection of as small a quantity of sodium chloride as 2–3 parts per 10,000 of water (Matthes and Wagner, Arch. Pharm. 1903, 241, 241). It has been used in the determination of ethyl alcohol in water (Wagner and Schultze, Zeitsch. anal. Chem. 1907, 46, 508; Andrews, J. Amer. Chem. Soc. 1908, 30, 353); in the detection and estimation of methyl alcohol in aqueous ethyl alcohol (Leach and Lythgoe (*ibid.* 1905, 27, 964); in the estimation of dextrose (Wagner and Rinck, Chem. Zeit. 1906, 30, 38); in the examination of beer (Ackermann, Zeitsch. ges. Brauw. 1905, 28, 259; 1906, 29, 145; Barth, *ibid.* 1905, 28, 303; Stanek and Miskovsky, *ibid.* 1910, 33, 145); in the detection of watered milk (Matthes and Müller, Zeitsch. öffentl. Chem. 1903, 9, 173; Leach and Lythgoe, J. Amer. Chem. Soc. 1904, 26, 1195; Ackermann, Zeitsch. Nahr. Genussm. 1907, 13, 186; Mai and Rothenfusser, *ibid.* 1908, 16, 7; 1910, 19, 737); in the determination of alkaloids (Utz, Chem. Zeit. 1909, 33, 47), and in the medical examination of urine and blood serum.

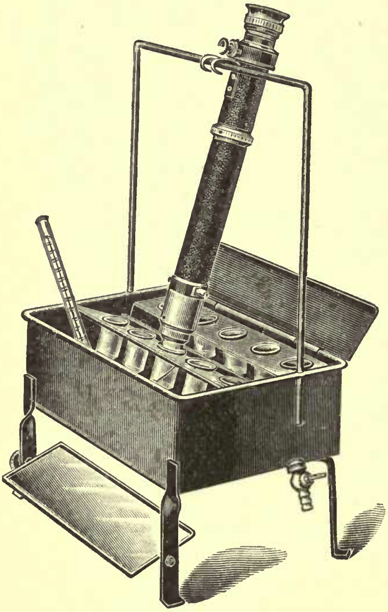


FIG. 8.

Other refractometers. In addition to the instruments described above, there are others which have been proposed for use in analytical work. A short reference to these refractometers must suffice.

Amagat and Jean's oleo-refractometer (*see* Muter, Analyst, 1890, 15, 87; Richmond, *ibid.* 1892, 17, 221; Pearmain, *ibid.* 1895, 20, 134) is a differential instrument, the essential parts of which are a collimator, a telescope, and an intermediate metallic vessel, provided with plate-glass sides, and filled with some standard oil. In the middle of this vessel there is a silver receptacle, with glass sides placed at a suitable angle, so as to form a prism. The field is divided into a light and a dark part by means of a shutter, and the position of the edge of this shadow varies with the refractive power of the oil which is put in the inner receptacle. The shutter is so adjusted that when the standard oil is put both in the inner and the outer vessels the edge of the shadow is at the zero of the scale in the telescope. When another oil is put in the inner receptacle, the edge of the shadow is displaced to a characteristic position either right or left of the zero.

In Tornöe's apparatus for determining the refraction of beers (*see* Ling and Pope, J. Fed. Inst. Brew. 1901, 7, 170) a modification of Hallwachs' prism is employed, consisting of a rectangular glass trough divided down the middle by a glass partition, the sides of which are parallel to one another and perpendicular to the end faces. The trough, containing beer in one division and water in the other, is placed on a spectrometer stand, and is illuminated at one end by sodium light. The position of the limiting ray which passes through from the water to the beer is ascertained by a telescope supported on the spectrometer stand and moving round a graduated circle. The trough is then rotated through 180° and the position of the limiting ray, now on the other side of the partition, is determined. From the angle between the two limiting rays the refractive index of the beer can be readily ascertained, and when the refractive index and gravity of the beer are known, the percentages of alcohol and extract can be estimated.

A direct-reading refractometer, suitable for the examination of oils or aqueous solutions, has been designed by Féry (Compt. rend. 1891, 113, 1028; 1894, 119, 332). The principle on which the apparatus is based is to annul by means of a solid prism of variable angle the deviation produced in a prism of the liquid under examination. The two prisms are united in one cell, two plano-convex lenses being so cemented together, with the curved faces outwards, that a wedge-shaped space is enclosed. In a form of the apparatus made by Hilger this space is enclosed by two wedge-shaped pieces of glass, and the annulling of the deviation produced in the cell is effected by two plano-convex lenses which form the opposite faces of a surrounding cell filled with water (*see* Fig. 9). The cell fits in a brass mount with two narrow apertures, 3 mm. high, and one above the other. The lower aperture allows the rays to pass through the base of the cell, which is entirely of glass and acts like a single plane parallel plate; the upper aperture allows those rays to pass which traverse the liquid. The deviation produced by the liquid in the cell is corrected by moving the cell and its mounting at right angles to the optical axis of the instrument, and from the extent of this lateral movement the index of refraction of the liquid may be deduced. The scale of the instrument, giving the index of refraction directly, extends from $n_D=1{\cdot}3300$ to $n_D=1{\cdot}6700$, and the apparatus gives the refractive index with an accuracy of nearly one unit in the fourth decimal place.

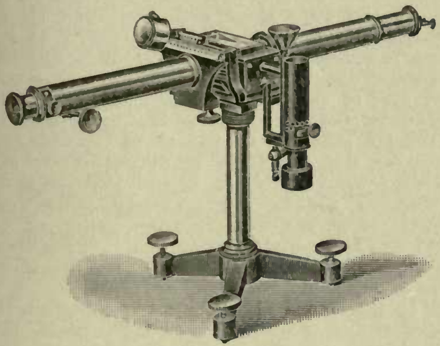


FIG. 9.

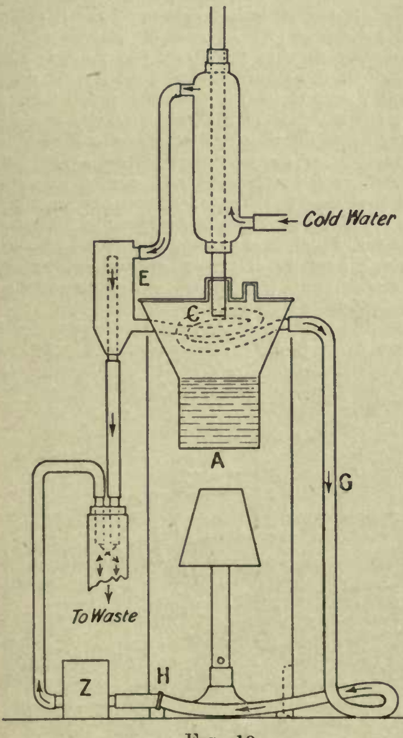


FIG. 10.

Supply of water at constant temperature for refractometers. Reference has already been made to the necessity, in the accurate refractometric investigations of fluids, of keeping the temperature constant. A supply of water at constant temperature may be obtained by running a stream of tap water (the temperature of which is generally constant over a considerable period) at a steady regulated pressure through a heated spiral. Various forms of apparatus have been devised for this purpose (Pulfrich, Zeitsch. Instrumentenkunde, 1898, 18, 49; Thorpe, Chem. Soc. Trans. 1904, 85, 257; von Heygendorff, Chem. Zeit. 1909, 33, 244; Hackman, Chem. News, 1910, 102, 192). The apparatus devised by Thorpe is shown in the adjoining sketch. A is a steam-generating vessel, through the upper part of which there passes the copper or 'compo' tubing C. The stream of water is heated in C, and thereafter passes through the pressure tubing G to the refractometer Z, the rate of flow being regulated by the screw clamp H. E is an arrangement for maintaining a constant head of water at the point of entrance to the coil. The apparatus can be brought into action very quickly, and gives under ordinary conditions a stream of water which does not vary more than 0·1° or so throughout the day

If a supply of tap water at steady temperature should not be available, it is best to circulate water from a constant temperature bath through the refractometer and back to the bath. This is conveniently effected with the help of a small rotary pump, such as that described by Lowry (Trans. Faraday Soc. 1907, 3, 119).

J. C. P.

REFRIGERATING AND ICE-MAKING MACHINERY. A refrigerating machine is a reversed heat engine in which energy is converted into heat, its function being to take heat from a body below the normal temperature and impart it to a hotter body. According to the second law of Thermodynamics, it is impossible for a self-acting machine unaided by any external agency to convey heat from one body to another at a higher temperature; therefore a refrigerating machine requires the application of energy. In fact, in working from a lower to a higher temperature an ideally perfect refrigerating machine requires the application of exactly the same quantity of energy as is given off by a perfect heat engine working from the higher to the lower temperature, and the quantity of heat rejected is the quantity of heat taken in at the lower temperature *plus* that due to the added energy. We can therefore define the coefficient of performance of a perfect refrigerating machine working between any two known temperatures.

If Q_1 is the quantity of heat taken in at the lower temperature T_1, Q_2 the heat given out at the higher temperature T_2, and $W=Q_2-Q_1$ the energy applied, all expressed in thermal units, the efficiency of the process is $\frac{Q_1}{Q_2-Q_1}$, or in a perfect refrigerating machine $\frac{T_1}{T_2-T_1}$. This is the ideal efficiency or co-efficient of performance for any temperature range, and it is independent of the working substance employed. The following table gives the co-efficient for several temperature differences:—

TABLE I.

T_1 Temperature at which heat is extracted in degrees C.	T_2 Temperature at which heat is rejected in degrees C.					
	10	15	20	25	30	35
−20	8·433	7·23	6·325	5·63	5·06	4·61
−15	10·32	8·61	7·38	6·45	5·74	5·16
−10	13·15	10·51	8·766	7·52	6·575	5·85
−5	17·86	13·4	10·72	8·933	7·66	6·7
0	27·3	18·2	13·65	10·92	9·1	7·8
5	55·6	27·8	18·532	13·9	11·12	9·266

It is, of course, not to be expected that such efficiencies are to be obtained in practice. In an actual machine there are many sources of loss, mechanical and otherwise, and allowance must be made for losses due to transmission in taking in the heat and in discharging it. The very nature of such transmission necessitates a difference of temperature, so that the low temperature produced by a refrigerating machine must be lower and the high temperature higher than the temperature of the body from which heat is to be taken and that of the body to which the heat is to be rejected. This alters the ratio between T_1 and T_2-T_1 and reduces the efficiency.

Two principal types of refrigerating machines are in use at the present time :—

1. That in which atmospheric air is cooled when under compression, and by subsequent expansion in the performance of work.

2. That in which heat is abstracted by the evaporation of a more or less volatile liquid.

In compressed air machines, which are now little used, ordinary atmospheric air is compressed and heated, due to the conversion into heat of mechanical energy expended in compression. The hot compressed air is then reduced in temperature by passing it through a vessel in which cold water is circulated, after which the cooled compressed air is expanded to about atmospheric pressure doing work behind a piston, and is further cooled owing to the conversion of heat into work. There is no change in physical state, and the sensible temperature of the air is raised by the heat of compression and lowered by the work done in expansion. For this reason, and owing to the fact that the weight and specific heat of air are so low, the difference between T_1 and T_2 is very great. Moisture in the air influences the final temperature owing to the heat given off in condensation and freezing. With this type of machine refrigeration is generally effected by discharging the cold air directly into the room or vessel to be cooled ; but sometimes the air is used in a closed circuit, the cooled air being passed through pipes placed in the room, and then taken back to the machine to be used over again. In either case the cooling effect is produced by the actual heating of the expanded and cooled air, and owing to the high temperature of compression in relation to the temperature of the cooling water and the low temperature of the discharged air in relation to the temperature of the room, the co-efficient of performance is very low. Were it practicable to construct and apply compressed-air machines dealing with very large volumes of air without undue losses, so that the final temperature of the compressed air is only slightly above that of the cooling water and the temperature of discharged air only slightly below that desired to be produced, we should then have efficiencies approximating to those given in Table I. In practice the air is compressed to about 50 lbs. above the atmosphere and discharged at a temperature approaching 149°C. (300°F.). It then passes through coolers, where it is reduced to within about 3°C. (5·4°F.) of the initial temperature of the cooling water and is deprived of a portion of its moisture, and is then expanded behind a piston to a little above atmospheric pressure and discharged at a temperature of about −57°C. (−70°F.). The compression and expansion pistons are connected, and the difference in power expended in compression and that given back in expansion, *plus* friction, is supplied by a steam-engine or any other source of power.

In the second class, for many years small hand-worked machines have been made, in which the evaporation of water under a high vacuum is employed; and in France the same machine, but on a large scale and using a vacuum produced by a steam injector, has been fitted on board war vessels for the cooling of magazines in which a comparatively high temperature is required. For industrial purposes, however, although it is theoretically possible to work with any liquid, practically all machines of this type work either with ammonia (NH_3), carbon dioxide (CO_2), or sulphur dioxide (SO_2), as the refrigerating agent. Of these ammonia is most largely used, because, owing to its physical properties, it gives the greatest heat elimination for a given expenditure of power. In all cases heat is abstracted by evaporation of the agent, the vapour being compressed and condensed, and the liquid used over again. Ammonia machines are also made in which the vapour is absorbed by water, which is subsequently heated and the ammonia evaporated off and condensed. These are respectively known as 'compression' and 'absorption' machines.

A diagram of a compression machine is shown in Fig. 1. There are three principal parts: refrigerator or evaporator, compressor, and condenser. The refrigerator usually consists of a coil or a series of coils connected at

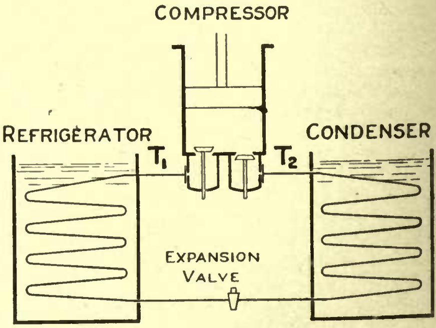


FIG. 1.

one end with the suction of the compressor, the delivery from the compressor being connected with the condenser, which also consists of a coil or series of coils. The refrigerator coils are surrounded with the substance to be cooled, and around the condenser coils cooling water is circulated. The bottom of the condenser coils is connected to the refrigerator coils by a pipe in which is a valve for regulating the quantity of liquid passing from the condenser to the refrigerator. The machine being in action, the refrigerating liquid flows into the refrigerator, in which the pressure is maintained so as to give the desired temperature of evaporation, and as this temperature is always below the temperature of the substance outside the coils, heat passes in from the outside, and causes the liquid to evaporate at the temperature T_1, the vapour being continually drawn off by the pump which compresses and delivers it into the condenser at the temperature T_2, which is somewhat above that of the cooling water. In the condenser heat passes from the compressed vapour into the water, the vapour being condensed, and the liquid which collects at the bottom returns through the regulating valve into the refrigerator. It will thus be seen that the essential difference between a compressed air machine and a machine using a condensable vapour is that, in the one case, heat is taken in and rejected by raising and lowering the sensible temperature of the air; and, in the other, the heat is taken in and rejected at constant temperature during the change in physical state of the agent. Consequently the results obtained with a vapour-compression machine must approach the ideal co-efficient of performance much more nearly than those obtained with an air machine. By properly arranging the surfaces in refrigerator and condenser there need not, as a rule, be more than about 6°C. (11°F.) difference between the temperature of evaporation and that of the liquid to be cooled, and between the temperature of condensation and that of the cooling water leaving the condenser; but these differences depend on the design and construction of the parts. In cooling insulated rooms the difference between the temperature of the air and the evaporating liquid is usually about 8°C. (15°F.).

Referring to Fig. 1, it will be seen that the liquid passes from the higher pressure and temperature of the condenser to the lower pressure and temperature of the refrigerator without performing external work, and in this respect the cycle differs from that of a reversed perfect heat engine. The liquid enters the refrigerator at condenser temperature, and before any useful refrigerating work can be performed it must be reduced to the refrigerator temperature by the evaporation of a part of its own quantity. The amount of this lost work is dependent on the relation between the latent heat of evaporation and the specific heat of the liquid, and varies according to the liquid used. It is smaller in NH_3 than in CO_2 and SO_2, and it is largely for this reason that machines employing NH_3 are so much used. Also with CO_2, which has a critical temperature of 31·4°C. (88·4°F.), the loss increases rapidly as the cooling water temperature rises, and beyond the critical temperature the cooling effect in the refrigerator is not produced under constant temperature, but by the actual heating of the vapour which on its way from the condenser has been cooled by the performance of internal work in expanding through the regulating valve from condenser to refrigerator pressure. The critical point of NH_3 is 136°C. (266°F.), a temperature never approached in refrigerating machines, so that when the plant is properly charged ammonia always enters the refrigerator in the liquid form. In cooling brine to −7°C. (20°F.), and with cooling water at 15·5°C. (60°F.), a well-designed compression machine of medium size driven by a steam-engine using 7 kilos. of steam per I.H.P. hour will abstract about 316 calories per kilo. of steam (375 B.T.U. per pound).

In absorption machines ammonia is the refrigerating agent, but there is no compressor. The vapour from the refrigerator passes over or through cold water which absorbs it, and the liquid is then pumped into a vessel in which it is heated by steam, and the ammonia driven off into the condenser. A complete absorption plant consists of a generator containing tubes to which live or exhaust steam is supplied at suitable pressure according to the temperature of the condensing water, an analyser, a rectifier, a condenser, a refrigerator, an absorber, and a pump for forcing the strong liquor produced in the absorber back through a heat interchanger into the analyser, where, meeting with the vapour rising from the generator, the ammonia is driven off, the water falling back into the generator. The process is thus carred on continuously. The condenser and refrigerator may be of precisely similar construction to those of a compression machine, the difference lying entirely in the mode of recovering the ammonia. In an absorption plant the only moving part is the strong liquor pump. In evaporating the ammonia, the latent, as well as part of the sensible heat of the steam is utilised in the generator, but much heat is required on account of having to drive off the ammonia from the water by which it has been absorbed, each kilo. requiring about 462 calories, whereas the latent heat of ammonia at the condenser temperature is only about 297. The co-efficients of performance as given in Table I. are not applicable to absorption machines, and in estimating their efficiency it is usual to take the ratio between the heat given off by the steam condensed in the generator and that abstracted in the refrigerator. One kilo. of steam supplied to a generator of an absorption plant will abstract about 280 calories in the refrigerator when cooling brine to −7°C. (20°F.) and with cooling water at 15·5°C. (60°F.).

Refrigerating machinery is used for the production of ice, for the preservation of perishable foods in cold stores on land and on board ship, and for cooling liquids and gases. The application is the same in compression and absorption machines. Ice is sometimes made by freezing the water on coils and surfaces in which the refrigerating agent is evaporated, but more generally the machine in the first instance cools an uncongealable brine, which is circulated through or around the freezing plates or cans. If clear ice is desired, the water must be agitated during freezing, or distilled water must be used. For the cooling of stores the air may be directly cooled by pipes called direct expansion pipes, in which ammonia or other liquid is evaporated, or by pipes through which cold brine is circulated, or by a circulation of air previously cooled in a special cooler.

One of the earliest applications of refrigerating machinery was for the separation of paraffin from shale and other oils, the oil containing paraffin in solution at ordinary temperature being passed over cold surfaces, which caused the paraffin to crystallise out. In the same way naphthalene and other substances can be separated from gases, and by having two or more supplies of the cooling agent at different temperatures any gas can be subjected to fractional condensation. Oils are artificially cooled and treated in filter presses to separate the stearin. In the manufacture of margarine very rapid cooling and separation of the residual milk is essential. The dry process in which the liquid margarine passes on to a revolving drum cooled by brine is now superseded to a large extent by the use of a plentiful supply of cold water applied in the form of a jet, so that the stream mixes intimately with the hot liquid margarine and immediately cools and washes it.

In the manufacture of potassium chlorate, the residual liquor which was formerly allowed to run to waste is now cooled to a temperature of about −26°C. (−15°F.), and a large proportion of the chlorate is recovered. The liquid is cooled in a tank by direct contact with expansion pipes, the crystals falling to the bottom. The cold liquor after treatment passes through an interchanger and partially cools the new charge on its way to the crystallising tank. There are many other applications of refrigerating machinery for assisting crystallisation (carbolic acid, for instance), and some years ago an attempt was made to use it in the crystallisation of common salt in place of the evaporation process. In the ammonia soda process the refrigeration is employed to separate ammonium chloride from the liquor. In each case the actual cooling surfaces must be arranged to suit the material to be cooled, and, when possible, it is of course economical to cool the new charge by the cold spent liquor. In beet sugar manufacture to increase the yield it is customary to use caustic strontia to form strontium saccharate, which is separated by filtration from the molasses. On cooling the strontium saccharate to about 5°C. (40°F.) it is split up into sugar and caustic strontia, the latter being used over again. The manufacture of the most important class of aniline dyestuffs, the azo colours, is largely dependent upon refrigeration. In the explosives industry, refrigeration finds application in checking chemical reaction and spontaneous decomposition, to which many nitro explosives are subject at high temperature. Other applications of refrigeration are in the liquefaction of chlorine which at atmospheric pressure requires a temperature of about −40°C. (−40°F.), and the cooling of viscose in the manufacture of artificial silk. In brewing and many other industries large quantities of cold water are required, and in most instances refrigerating machinery is used. Refrigeration is also used in controlling the fermentation of beer, yeast, tobacco, cheese, cream, and other substances, and in drying air. In the mercerising process it has been found advantageous to cool the caustic alkalis. The Hoepfner process of producing pure sodium sulphate by crystallisation from acid solutions necessitates the use of brine at a temperature of about −4°C. (25°F.), and in the same process large quantities of chlorine are produced in the electrolytic production of zinc, the chlorine usually being condensed by means of a refrigerating machine.

Liquid air, oxygen, nitrogen, and hydrogen are also produced by means of low temperatures, but the apparatus employed differs from those considered in this article, and is dealt with under a separate heading.

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T. B. L.

REGINA PURPLE. *Acetate of o-tolyl-p-rosaniline* $C_{28}H_{25}N_3O_4$ *v.* TRIPHENYL METHANE COLOURING MATTERS.

REGULUS. An alchemistic term signifying *the little king*, apparently first applied to antimony. Now used in metallurgy to denote an impure metal obtained from its oxide or sulphide by fusion with a reducing agent.

REHEATING. A metallurgical term mainly applied to the operation of heating puddled bars to a welding heat preparatory to passing them through rolls.

REICHARDTITE. A massive variety of epsomite, $MgSO_4,7H_2O$, found at the Stassfurt salt deposits (Krause, Arch. Pharm. 376, 41).

RENADEN *v.* SYNTHETIC DRUGS.

RENOFORM *v.* SYNTHETIC DRUGS.

RESAZURIN (*Azoresorcin*, *Diazoresorcin*, *Resazoin*). An indicator which gives a blue colour with alkalis and a red with acids.

It is prepared by dissolving 4 grms. resorcinol in 300 c.c. dry ether and adding 3–4 c.c. of fuming nitric acid (sp.gr. 1·25), the temperature being kept at −5° to −8°. The solution is allowed to stand in a cool place for two days and the dark coloured crystals separated from the mother liquor and washed with ether and water until the washings have a pure blue colour (Crismer, Bull. de l'Assoc. Belg. des Chimistes, 10, 22; J. Soc. Chem. Ind. 1896, 618).

Resazurin occurs in reddish-brown crystals, slightly soluble in water, more soluble in alcohol, and easily soluble in ethyl acetate. It is a monobasic acid, but its exact composition is unknown.

It is prepared for use by dissolving 0·2 grm. in 40 c.c. of N/10 ammonia and diluting to 1000 c.c. The solution has a deep blue colour by reflected light, but is reddish by transmitted light; it is quite stable. About 3 drops of this solution suffice for the titration of 200 c.c. of liquid.

Resazurin is specially useful for titrating N/10 solutions of borax, to which litmus or phenol-phthalein is not sufficiently sensitive, and is generally very sensitive to alkalis. It cannot be used for nitric acid or weak organic acids (*see* Lemoine, Bull. Assoc. Belg. Chim. 13, [4] 178, 185, 188; and 187; J. Soc. Chem. Ind. 1899, 608, 610, 611, 614).

RESINS. Resins constitute a class of vegetable or, rarely, animal products which are solid or semi-solid, insoluble in water, but generally soluble in alcohol, ether, and volatile oils. They nearly all begin to soften at temperatures much below their melting-points. They are often left by the spontaneous evaporation of oleoresinous juices which exude either naturally or by incision from the trunks of trees. A number are found as minerals, but these are undoubtedly the product of extinct vegetation. Others are extracted from various parts of plants by such solvents as alcohol and ether. This article excludes those resins which contain benzoic or cinnamic acid (*balsams*), those which appear in commerce admixed with gum (*gum resins*) or volatile oil (*oleoresins*), and those which consist of hydrocarbons allied to *petroleum.* It is perhaps to be regretted that it is necessary to retain such a classification as this, based as it is upon commercial or botanical considerations, or at best upon physical distinctions of solubility. Chemical inquiry, however, has not been carried far enough yet to make a more scientific arrangement possible, and indeed, so widely do the various resins that have been studied differ from one another chemically that it seems likely that as a class they will ultimately disappear, being taken to fill in gaps here and there in the growing structure of organic chemistry.

We shall here treat of the more important representatives of this group of substances. For those which are less known, see the various Reports on Botanical Economics, and Museum Catalogues. On the formation of resins see Heldt (Annalen, 63, 48), Wiesner (Sitz. Ber. K. Akad. Wien. 52, 2, 118), Barth (Zeitsch. Chem. 1867, 508), and Tschirch (Arch. Pharm. 243, 81); their composition and behaviour towards reagents, Rose (Annalen, 13, 174), Johnston (*ibid.* 44, 328); the compounds formed by the action of melted potassium hydroxide, Hlasiwetz and Barth (*ibid.* 134, 265; 138, 61; 139, 77); their neutralisation or saponification coefficients when treated with a standard solution of caustic alkali, Kremel (Zeitsch. anal. Chem. 26, 262; Pharm. J. [iii.] 17, 547); their respective iodine absorption numbers, Williams (Chem. News, 58, 224); determination of their methoxyl equivalents, Bamberger (Monatsh. 11, 84), and on the systematic identification of resins, see Hirschsohn (Pharm. Zeit. 16, 81; 24, 529; Zeitsch. anal. Chem. 17, 256); Dieterich (Pharm. Zentsh. 37, 424), and Schmidt and Erban (Monatsh. 7, 665). See also Tschirch, Die Harze und die Harzbehälter, Leipzig, 1900.

Alouchi, or **Aluchi Resin.** A resin imported from Madagascar. It is friable, dirty-white externally, blackish and marbled within, and has a bitter, peppery taste. It was examined by Bonastre (J. Pharm. Chim. 9, 180; 10, 1), who found it soluble in cold alcohol to the extent of 68·12 p.c. A further portion, 20·45 p.c., dissolved in hot alcohol. It contains a small proportion (1·6 p.c.) of essential oil. *V.* also Vauquelin (Ann. Chim. Phys. ii. 72, 299).

Arnica Resin, *Arnicin.* The root of *Arnica montana* (Linn.), a compositous plant inhabiting the northern and central regions of Europe and America (Bentl. a. Trim. 158), contains a resinous substance to which the name *arnicin* has been given, together with *gum, wax, inulin* 10 p.c., *volatile oil,* and an alkaloid (?) *arnicine* (Bastick, Pharm. J. 10, 386), and other constituents. The resinous compound arnicin was isolated by Walz (Neuer. Jahresb. Pharm. 13, 175; 14, 79; 15, 329). It is yellow, amorphous, has an acrid taste, is soluble in alcohol, ether, and alkalis, and is precipitated from the alcoholic solution by water. Analysed, it gave numbers corresponding with the formula $C_{20}H_{30}O_4$. It may possibly prove to be a glucoside. For another constituent to which the name 'arnicin' has been given, *v.* Parvesi (J. 1859, 584).

Betula Resin, *Betulin.* The outer bark of the birch tree, *Betula alba* (Linn.), yields a resin. Löwitz, in 1788, described it (Crell's Annalen, 2, 312), and it has been further examined by Hünefeld (J. pr. Chem. [i.] 7, 53), Hess (Annalen, 29, 135), Mason (Berzelius Jahresb. 12, 248), Stähelin and Hofstetter (Annalen, 51, 79), Housmann (*ibid.* 182, 369), and others. Betulin melts at 258°, and has the formula $C_{36}H_{60}O_3$.

Capsicum Resin. The fruits of *Capsicum minimum* (Roxb.) and *Capsicum annuum* (Linn.), constituting respectively the small and large red or cayenne pepper pods of commerce, yield a *resin* to which the acrid property of the pods was once attributed. The other important constituents are a *volatile oil,* a volatile alkaloid, *capsicine,* which resembles coniine (Felletár, J. Pharm. Chim. 1870, 347; Thresh, Pharm. J. [iii.] 6, 941), and an intensely active acrid, crystalline compound discovered by Thresh, *capsaicin,* to which the pungency of cayenne pepper is now ascribed (*ibid.* [iii.] 7, 21, 259, 473; 8, 187). *V.* also Meyer (Pharm. Zeit. 1889, 130), Pabst (Arch. Pharm. 230, 108), Nessler (Zeitsch. Nahr. Genussm. 11, 661), Micko (*ibid.* 1898, 818; 1899, 411), Nelson (Chem. News, 1911, 103, 111). Capsaicin has the formula $C_9H_{14}O_2$. It does not possess basic properties. It melts at 64·5° (Nelson), sublimes at 115°, and has a sp.gr. of 1·060. Most solvents, including sulphuric and glacial acetic acids, dissolve capsaicin; but it is insoluble in water, and is thrown out of its solution in alkalis by a stream of carbonic dioxide. The fruits of *Capsicum minimum* (Roxb.) contain about 20 times as much capsaicin as those of *Capsicum annuum* (Micko, *l.c.*).

Castoreum Resin. The dried preputial follicles of the beaver, *Castor fiber* (Linn.), are used in medicine as a nervous stimulant or anti-spasmodic (Pereira, Mat. Med. 1853, 2, 2266). Castor contains a *resin,* 1–2 p.c. of *volatile oil,* and a neutral crystalline substance, *castorin.* If castor be treated with hot alcohol, either with or without previous admixture with lime, a solution results which, on cooling, deposits castorin in crystals, and from the mother-liquor of which the resin may be obtained by the addition of water. Castorin was discovered by Bizio (Arch.

Pharm. 11, 112), and further investigated by Valenciennes (Pharm. J. 1861, 329). It is neither acid nor basic, and assumes the form of easily-fusible needles which possess only in a faint degree the odour and taste of castor. The activity of castor resides in the resin, which, having been precipitated by water from the alcoholic solution, from which the castorin has been separated, may be purified by re-solution in alcohol and re-precipitation by water. The yield varies very much, some specimens of castor giving as much as 58 p.c., and others not more than 14 p.c. Castor resin is nearly black. It is brittle, and is insoluble in ether. It possesses the bitterness and acridity of castor in a very high degree. The volatile oil obtained, to the extent of 1 or 2 p.c., by distilling castor with water is pale-yellow and viscid, is nearly insoluble in water, but soluble in alcohol, and possesses the odour of the drug. With regard to the supposed presence of an *alkaloid* in castor, *v.* Reuter (Pharm. Centh. 1889, 305). Many other constituents, in small proportion, have been announced from time to time as occurring in castor, such as bile, salicin, benzoic acid, and phenol.

Colophony (*Common Resin*; *Rosin*; *Resina*, Br. Ph.; *Colophane*, Fr.; *Kolophonium*, Ger.). Colophony is the residue which remains after the volatile oil has been removed by distillation from the oleoresins, the crude turpentines which exude from various species of coniferæ. It varies somewhat, according as it is derived from the one or the other species, and with the method employed for its production. The browner resins are mostly of American origin, from *Pinus palustris* (Mill.); whilst those of a lighter colour come by way of Bordeaux, being the yield of *Pinus Pinaster* (Solander), found in the districts of the Landes and the Gironde. It varies in colour from pale amber to dark red-brown. The 'white resin' of commerce owes its light-yellow colour to a slight opacity, due to the presence of small quantities of water.

Colophony is a very brittle solid with a glassy fracture. It has a faint odour of turpentine, and scarcely any taste. It is heavier than water, in which it is insoluble. Its sp.gr. is generally 1·07. Ether, chloroform, acetone, benzene, volatile and fixed oils dissolve it readily, and at 60° it is soluble in its own weight of alcohol or glacial acetic acid. It is soluble in alkalis. It softens at 80°, and melts variously from 100° in some specimens to 135° in others. Heated to higher temperatures it yields gaseous products and a distillate of *resin oil*, but in a current of steam above 200° colophony may be distilled without any appreciable change.

American colophony consists essentially of a resin acid, *abietic acid* $C_{19}H_{28}O_2$ or $C_{20}H_{30}O_2$ (Maly, Annalen, 149, 115, 161, 244; Liebermann, Ber. 17, 1884; Haller, *ibid.* 18, 2165; Mach, Monatsh. 14, 186; 15, 627; Fahrion, Zeitsch. angew. Chem. 14, 1197, 1221, 1252; Levy, *ibid.* 18, 1739; Ber. 39, 3043). Varying figures for the melting-point of abietic acid ranging from 139° to 165° have been given by different observers, whilst Levy, by vacuum distillation and repeated crystallisation from methyl alcohol, obtained a product melting at 182°.

Tschirch and Studer (Arch. Pharm. 241, 495) by treating an alcoholic solution of colophony with alcoholic lead acetate obtained two isomeric resin acids. The first, *α-abietic acid*, the lead salt of which is insoluble in alcohol, is a monobasic acid; it softens at 143° and melts completely at 155°. The second, *β-abietic acid*, softens at 145°, is completely melted at 158°, is monobasic and is not precipitated by alcoholic lead acetate. From the ethereal solution of the resin, a third isomeride, *γ-abietic acid*, was extracted by aqueous sodium carbonate: it melted at 153°–154°. After removing the acids, about 5–6 p.c. of *resene* remained as a brown mass that softened in the hand. (For the constitution of abietic acid *v.* Easterfield and Bagley (Chem. Soc. Trans. 85, 1238); Tschirch and Studer (Arch. Pharm. 241, 523).)

When colophony dissolves in alkali, an alkaline abietate, or *resin soap*, is formed. This is largely employed as an admixture in the manufacture of the commoner soaps. Heated to redness colophony evolves a mixture of gases, which burns with a bright flame, and it has been proposed as a source of illuminating gas. It enters largely into the constitution of the less-esteemed varnishes, is used for the caulking of ships, for cements, as a flux in the soldering of metals, and in pharmacy it enters into many ointments and plasters.

The *resin* or *rosin oil* obtained by the dry distillation of resin is widely made use of, and its chemical constituents are being more and more studied. It consists essentially of a mixture of hydrocarbons and fatty acids. Generally it is separated into two portions, the lighter spirit that first comes over being collected apart from the heavier oil, which distils last. The lighter spirit is used as a substitute for oil of turpentine, while the heavier is employed as a lubricant and in soap-making. The lighter *resin spirit*, boiling below 360°, contains, according to Renard (Ann. Chim. Phys. [vi.] 1, 223) the following compounds: pentane, boiling from 35° to 38°, amylene (35°–40°), the hydrocarbons C_6H_{14}(64°–66°) and C_6H_{12}(67°–70°), hexahydrotoluene (95°–98°), tetrahydrotoluene (103°–105°), toluene (111°), hexahydroxylene (120°–123°), tetrahydroxylene (128°–130°), xylene (136°), hexahydrocumene (147°–150°), the hydrocarbon C_9H_{16} (155° ?), cumene (151°), terpenes (154°–157° and 171°–173°), hexahydrocymene (171°–173°), cymene (175°–178°), *m*-ethylpropylbenzene (193°–195°), the hydrocarbon $C_{16}H_{28}$ (about 260°), *iso*butyric aldehyde (60°–62°), valeric aldehyde (96°–98°), also *iso*butyric acid and valeric acid. Colophene (318°–328°), the compound formed by polymerising turpentine oil by means of sulphuric acid, is also a constituent of resin spirit (Deville, Annalen, 37, 193). There is little doubt that the colophene found in resin spirit by Deville is identical with *abietene* $C_{18}H_{28}$, a hydrocarbon obtained by Easterfield and Bagley (Chem. Soc. Trans. 85, 1244) by the distillation of crystalline abietic acid. The heavier *resin oil*, boiling above 360°, consists of hydrocarbons together with a mixture of acids and phenols and much undecomposed colophony. For other constituents of resin oil see Tilden (Ber. 13, 1604), Kelbe (Annalen, 210, 12), Kelbe and Lwoff (Ber. 16, 351), and Lwoff (*ibid.* 20, 1020), Brownsword and Cohen (J. Soc. Chem. Ind. 1890, 16), Tschirch and Wolff (Arch. Pharm. 245, 1), Schultze (Annalen, 359, 129). The gases evolved during the distillation have been examined by Schiel (*ibid.* 115, 96). When the resin oil boiling from 103°–104° is allowed to stand in contact with air and water, a crystalline solid, *colophonium hydrate* is formed, having the composition $C_{10}H_{22}O_3,H_2O$. It melts at 106° and sublimes with some decomposition (Tichborne, Pharm. J. [iii.] 1, 302; Anderson, J. 1869, 787; Tilden, Ber. 13, 1604). According to Bischoff and Nastvogel (*ibid.* 23, 1919), the breaking up of colophony by destructive distillation is much simpler if the operation be performed under reduced pressure. In this case the products are chiefly two: one a hydrocarbon, $C_{20}H_{32}$, boiling at 218°–220° (30 mm.), which is probably colophene; the other, a liquid, which slowly solidifies to a mass of microscopic crystals having the composition $C_{40}H_{58}O_3$. This compound is, however, found by Easterfield and Bagley to be ordinary abietic acid, melting at 160°–165°. The distillation of colophony in superheated steam yields the same products as the distillation under reduced pressure.

When resin is distilled with lime, another series of compounds is produced (Fremy, Ann. Chim. Phys. [ii.] 59, 13; Bruylants, Ber. 8, 1463; 11, 448). For distillation of resin with sulphur, *v.* Currie (J. 1874, 921), Kelbe (Chem. Zentr. 1887, 1504), Vesterberg (Ber. 36, 4200); for products of the oxidation of resin with nitric acid, *v.* Schreder (Annalen, 172, 93) and Vogel (J. 1869, 785), and for distillation of colophony and resin oil under pressure, *v.* Kraemer and Spilker (Ber. 32, 2952, 3614; 33, 2265).

For methods of detecting the presence of resin oil in fixed, volatile or mineral oils, see Storch (J. Soc. Chem. Ind. 7, 136), Holde (*ibid.* 7, 526; 9, 419), Morawski (*ibid.* 8, 572), Chenevier (*ibid.* 9, 825), Baudin (J. Pharm. Chim. [v.] 23, 279), Gilbert (Chem. Zeit. 13, 1428), Grittner (Zeitsch. angew. Chem. 5, 265), Zune (Compt. rend. 114, 490), McIlhiney (J. Amer. Chem. Soc. 16, 385), Klimont (Chem. Zentr. 1895, i. 563), Cornette (L'Orosi, 19, 234), De Koningh (Chem. News, 77, 287), Halphen (J. Pharm. Chim. [vi.] 16, 478), Valenta (Chem. Zeit. 29, 807).

Resin is used largely as an adulterant. For methods for its detection and estimation, see—Resin in Soap: Senier (Amer. J. Pharm. [iv.] 4, 353), Gladding (Amer. Chem. J. 3, 416), Heiner (J. Pharm. Chim. [v.] 11, 434), Wright and Thompson (Chem. Soc. Proc. 2, 175), Grittner and Szilasi (Chem. Zeit. 10, 325), Morawski (J. Soc. Chem. Ind. 1888, 891; 1889, 592; Chem. Zeit. 12, 1321), Holde (J. Soc. Chem. Ind. 1889, 592), Twitchell (*ibid.* 1891, 804), Lewkowitsch (*ibid.* 12, 503), Landin (Chem. Zeit. 21, 25). Resin in Fats: Gladding (Amer. Chem. J. 3, 416), Focke (Chem. Zentr. 1886, 44), Landin (Chem. Zeit. 21, 25), Holde (Zeitsch. angew. Chem. 15, 650). Resin in Wax: Morawski, *l.c.*; Röttger (Chem. Zeit. 15, 45). For a method of testing colophony, *v.* Dieterich (Zeitsch. angew. Chem. 12, 915).

Common Frankincense (*Gum Thus*; *French Pine Resin*; *Galipot*, Fr.). The crude turpentine which concretes on the trunks of the French pine trees was scraped off and employed in pharmacy. The greater part of the *Gum Thus* of commerce is now, however, derived from the American pine trees, *Pinus palustris* (Mill.) and *Pinus Taeda* (Linn.). The French resin does not consist of abetic acid but of a group of nearly related pimaric acids. These have been investigated by Laurent (Ann. Chim. Phys. [ii.] 72, 34; [iii.] 32, 459), Maly (Annalen, 129, 94; 132, 253), Duvernoy (*ibid.* 148, 143), Strecker (*ibid.* 150, 131), Bruylants (Ber. 11, 448), Caillot (Bull. Soc. chim. [ii.] 21, 387), Liebermann (Ber. 17, 1884), Haller (*ibid.* 18, 2165), Vesterberg (*ibid.* 18, 3331; 19, 2167; 38, 4125; 40, 120), and by Henry (Chem. Soc. Trans. 79, 1151). For investigations of the natural resins, see *Turpentine* in article on OLEO-RESINS.

Copal Resin. Copal is the concrete exudated juice of various trees. It is obtained either directly from the trees or as a fossil resin buried in the earth in their neighbourhood. Fossil copal is a highly-prized variety. Copal comes from the East Indies, South America, New Zealand, and both the east and west coasts of Africa. Some copals are soft; these are obtained from Sumatra, Java, Molucca, the Philippines, and Australia, and they are soluble in ether. The hard copals, which do not dissolve in ether until they have undergone a chemical change, come by way of Calcutta from Zanzibar and the African coast, and by way of Bombay from Madagascar, Mauritius, and Bourbon. Hard copal varies in properties somewhat with the origin of the different resins which are known by that name; but generally it is of a light-yellow or brown colour, without taste or smell, and has always been prized for varnishes. It occurs in roundish or flattish pieces, more or less transparent, and breaks with a conchoidal fracture. The sp.gr. varies from 1·045 to 1·139, but it is generally between 1·059 and 1·072. In the crude state hard copal is insoluble in alcohol, and only partially soluble in ether or oil of turpentine. When, however, the crude resin is heated, gases are evolved, and a residue remains which dissolves readily in ether and oil of turpentine. In making varnishes, copal is melted and heated slightly, and hot turpentine slowly run into the melted resin.

Submitted to destructive distillation, copal yields a terpene boiling at 160°–165° and a heavier oxygenated oil (Schibler, Annalen, 113, 339). Friedburg (J. Amer. Chem. Soc. 12, 285, 392) finds that when copal is distilled, a terpene, probably limonene, comes over between 100° and 185°, and that above that temperature decomposition takes place until at 215° a dark residue remains. Wallach and Rheindorff (Annalen, 271, 308) find pinene and dipentene to be present in the oily distillate obtained by the dry distillation of copal.

Manilla copal is exported from the Philippine Islands. Much of the copal, however, which comes from the Philippines is produced in the Dutch East Indies and certain islands in Polynesia; but, in recent years, the greater part of the resin collected in the Dutch East Indies has reached European markets through Singapore and other ports and is known in commerce as 'Macassar,' 'Pontianac,' or Singapore copal. These copals are almost entirely obtained from the *Agathis loranthifolia* (Salisb.). They have been investigated by Tschirch and Koch (Arch. Pharm. 240, 202) and by Richmond (Philippine J. Sci. 1910 [A] 5, 177). Analytical constants are given by Coffignier (Bull. Soc. chim. [iv.] 3, 453), and the products obtained by destructive distillation and by oxidation have been investigated by Brooks (Philippine J. Sci. 1910 [A] 5, 203, 219).

The copal obtained from South America is collected mainly from the living trees, *Hymenaea Courbaril* (Linn.), but it is also found in the fossil form. It forms the 'Demerara animi' of commerce. (For description and solubilities of Demerara, Columbian, and Brazilian copals, *v.* Coffignier (Bull. Soc. chim. [iii.] 35, 1143).

Kauri copal is a fossil resin derived originally from the kauri pine, *Dammara australis* (Lamb.). It is found principally in New Zealand. Tschirch and Niederstadt (Arch. Pharm. 239, 145) found 100 parts of the resin to contain: *kauric acid* $C_{10}H_{16}O_2$, m.p. 192°, 1·5; *α- and β-kaurolic acids*, $C_{12}H_{20}O_2$, 48°–50°; *kaurinolic acid*, $C_{17}H_{34}O_2$, m.p. 128°–130°, and *kauronolic acid*, $C_{12}H_{24}O_2$, m.p. 86°–89°, 20–22; essential oil, 12·5; *kauroresene*, 12·2; bitter substance, 0·5–1 parts. The solubilities of the commercial varieties in different solvents are given by Coffignier (Bull. Soc. chim. [iv.] 5, 289).

East African copal, known in commerce as Zanzibar anime or Zanzibar copal, is collected in British, German, and Portuguese East Africa. It is a fossil resin found chiefly in localities from which copal trees have now disappeared. Examined by Stephan (Arch. Pharm. 234, 552), Zanzibar copal was found to contain two isomeric dibasic hydroxy acids, $C_{56}H_{88}O_8$, *trachylolic acid*, m.p. 165°, and *isotrachylolic acid*, m.p. 105°–107°, the former differing from the latter by being precipitated from alcoholic solution by lead acetate. Two resenes were also found to be present, *α-copalresene*, m.p. 75°–77°, soluble in ether, and *β-copalresene*, insoluble in ether and decomposing at 140° without melting. The resin contains 80 p.c. of trachylolic acid, 4 p.c. of the isomeride and 6 p.c. of the resenes.

West African copals are of very variable quality, the best sorts being fossil or semi-fossil whilst the medium and poorest qualities are procured from living trees. The best West African copals, at the present day, are those from Angola, Benguela, and the Congo. Sierra Leone and Accra copals are of medium quality, and Niger copal is the poorest. Inquiries made during the last few years in the British West African Colonies leave little doubt that Sierra Leone copal is obtained from *Copaifera Guibourtiana* (Benth.), Gold Coast or Accra copal from *Cyanothyrsus Ogea* (Harms.), and Niger copal from *Daniella oblonga* (Oliver) (Imp. Inst. Rep. No. 63, 171). For investigation of Kissel copal, *v.* Coffignier (Bull. Soc. chim. [iii.] 33, 169); Cameroon copal, Coffignier (*l.c.*); Tschirch and Rachwitz (Arch. Pharm. 245, 145); Accra copal, Coffignier (*l.c.*); Kahan (Arch. Pharm. 248, 443); Angola copal, Tschirch and Rackwitz (*l.c.*), Coffignier (Bull. Soc. chim. [iv.] i. 1131); Benin copal, Kahan (Arch. Pharm. 248, 433); Benguela and Congo copals, Coffignier (Bull. Soc. chim. [iv.] i. 1131); Engel (Arch. Pharm. 246, 293); copals from Nigeria and the Gambia (Imp. Inst. Rep. No. 63, 176); Loango copal, Willner (Arch. Pharm. 248, 265); Sierra Leone copal, Coffignier (Bull. Soc. chim. [iv.] i. 1131), Engel (*l.c.*), Willner (Arch. Pharm. 248, 285).

The acid and saponification numbers of several varieties of copals are given by Lippert and Reissiger (Zeitsch. angew. Chem. 1900, 1047); Worstall (J. Amer. Chem. Soc. 25, 860).

Dammara Resin (*East Indian Dammara Resin*; *Dammar Puti*). The dammar resins are obtained from species of *Hopea, Shorea,* and *Balanocarpus*, mainly in the Federated Malay States, Sumatra, and other Dutch East Indian Islands. Small quantities of dammar-like resins are obtained in India, but so far as European commerce is concerned these are of no importance (Imp. Inst. Rep. No. 63, 182). The resin exudes and dries on the trees in lumps of various shapes and sizes, and is collected. It is partially soluble in alcohol, more so in ether, and almost completely in fixed and volatile oils. It is entirely soluble in sulphuric acid. The resin has been examined by Dulk (J. pr. Chem. [i.] 45, 16); Schrötter (Pogg. Ann. 59, 72); Graf (Arch. Pharm. [iii.] 27, 97); Glimmann (*ibid.* 234, 584).

When crude dammar is treated with weak alcohol, a portion, about one-third, dissolves: this is the *α-resin* or hydrated *dammarylic acid* of Dulk. From the residue, absolute alcohol extracts the *β-resin* or anhydrous *dammarylic acid*. By treatment of the residue with ether, according to Dulk, a hydrocarbon *dammaryl* $C_{45}H_{72}$ is dissolved. Dammaryl is a tasteless, inodorous powder which softens at 145° and melts at 190°. When it is exposed to the air it undergoes oxidation until a substance is formed having the composition of the original resin. Graf, however, denies the presence of this hydrocarbon. Glimmann finds the resin to consist of *dammarolic acid*, a dibasic acid $C_{56}H_{80}O_3$, 23 p.c.; *α-dammar-resene* $C_{11}H_{17}O$, m.p. 65°, 40 p.c.; *β-dammar-resene*, m.p. 200°, 22·5 p.c. The β-dammar-resene consists of the portion of the crude resin which is insoluble in absolute alcohol. The ethereal oil obtained by distilling the resin with steam boils at 82°. (For description and analytical results of different varieties of dammar, *v.* Imp. Inst. Rep. No. 63, 182; Dieterich (Pharm. Centh. 40, 453; Coffignier (Bull. Soc. chim. [iv.] 9, 549), and for detection of colophony in dammar resin, Hirschsohn (Zeitsch. anal. Chem. 37, 456).

Dragon's Blood Resin. *Resina Draconis* (*Sangdragon*, Fr.; *Drachenblut*, Ger.). The name 'dragon's blood' has been employed from ancient times to designate various red resinous exudations, but it is chiefly applied now to the crimson-red resin which exudes and dries on the fruits of the rotany or rattan palm, *Calamus draco* (Willdenow), of the East Indies. The drug appears in commerce for the most part in two forms—the one consisting of sticks of resin wrapped in palm leaves, the *reed dragon's blood*; the other, the *lump dragon's blood*, being blocks or irregular-shaped masses (Flück. a. Hanb. 673). Dragon's blood has a sweetish, somewhat acrid taste, and melts at about 120°, when it is said to evolve benzoic acid. It dissolves in alcohol, benzene, chloroform, carbon disulphide, glacial acetic acid, and caustic soda. In light petroleum it is insoluble, and it dissolves but sparingly in oil of turpentine or ether. It is employed as a colouring agent in pharmacy, and for varnishes.

Among other resins to which the name dragon's blood has been given are: *Socotrine*

Dragon's Blood, obtained from trees of the genus *Dracœna* in the island of Socotra (Balfour, Pharm. J. [iii.] 14, 372); *Canary Islands Dragon's Blood*, derived from *Dracœna Draco* (Linn.); and *West Indian Dragon's Blood*, which is produced by *Pterocarpus Draco* (Linn.); and *Croton Draco* (Schlecht) (*v.* Flück. a. Hanb.). According to Dobbie and Henderson (Pharm. J. [iii.] 14, 361), who examined a large number of specimens, the dragon's blood of commerce consists of four distinct products. The *Calamus*, or East Indian resin, agreed with the characters given above, except that it was freely soluble in ether.

The dragon's blood imported in the form of sticks has been examined by Dieterich (Arch. Pharm. 234, 401). It melted at 70°. If the crude resin is extracted with ether, and alcohol added to the extract, *dracoalban* $C_{20}H_{40}O_4$ is precipitated. It is a white amorphous powder which softens at 192°–193° and decomposes above 200°. On evaporation of the solution after removal of the precipitate and extraction of the residue with light petroleum, *dracoresene*, $C_{26}H_{44}O_2$, a bright yellow amorphous resin, m.p. 74°, is obtained. The portion insoluble in light petroleum is a mixture of pure resins of a red colour—the *dracoresinotannol* salts of benzoic and benzoylacetic acids. The red resin consists mainly of dracoresinotannol benzoate. On hydrolysis, dracoresinotannol, $C_8H_9O{\cdot}OH$ is obtained as a bright brown amorphous powder which softens at 100°–105° and then decomposes without melting: 18·4 p.c. of plant remains and 8·3 p.c. of ash were also present.

Blyth and Hofmann (Chem. Soc. Trans. 2, 334) found toluene and styrene among the products of the destructive distillation of dragon's blood (*cf.* Glénard and Boudault, Compt. rend. 17, 503; 19, 505). When fused with potash the resin yields benzoic and *p*-hydroxybenzoic acids and phloroglucinol (Hlasiwetz and Barth, Annalen, 134, 283); distilled with zinc-dust, styrene, toluene, and other products (Bötsch, Monatsh. 1, 609), and by the action of nitric acid, oxalic and nitrobenzoic acids (Blumenau, Annalen, 67, 127).

Ergot of Rye Resin. Ergot contains a resin, to which at one time its activity was thought to be due (*v.* Ergot).

Eucalyptus Resin. Obtained from the leaves of *Eucalyptus Globulus* (Labill.). It is coloured carmine-red by sulphuric acid (Hartzer, Ber. 9, 314).

Fossil Resins. *Amber, Succinite, Bernstein.* A hard, generally yellow or orange resin thrown up by the sea, along the Baltic coast, especially in Prussia, and in smaller quantities throughout the world (*v.* Rose, Annalen, 28, 339). Amber is tasteless and brittle, and admits of a fine polish. It is much used as an ornament. It becomes negatively electric by friction. The sp.gr. of amber varies from 1·05 to 1·10, and it ranks 2 to 2·5 in the scale of hardness. There can be no doubt that amber is the fossil resin of extinct coniferæ (Göppert, *ibid.* 21, 71). The character of the insects which it includes, and which often render it very beautiful, are an evidence in support of this view.

Amber contains 0·24 to 0·48 p.c. of sulphur (Baudrimont, J. 1864, 538). When heat is applied to it there is evolved, in the first place, succinic acid, water, oil, and combustible gases; the residue is then soluble in alcohol and oil of turpentine. A further application of heat brings over a colourless oil, *oil of amber*, which, when the distillation is well managed, amounts to 28 p.c. of the original resin. Finally, when the temperature rises at the close of the operation, a yellow *wax* condenses. Oil of amber is a mixture of several hydrocarbons. The lighter portion is coloured blue by hydrochloric acid, and decomposed by sulphuric acid, whilst the heavier portion is unacted on by these reagents.

Tschirch and Aweng (Arch. Pharm. 232, 660) find that the portion of succinite soluble in alcohol consists principally of *succinoabietic acid* $C_{80}H_{120}O_5$, with a small proportion of the bornyl ester of this acid and some sulphur. The portion (70 p.c.) of succinite insoluble in alcohol is almost entirely composed of the succinate of a resin alcohol *succinoresinol*. Succinoabietic acid is crystalline and melts at 148°, and when fused with potash it yields succinic acid. Succinoresinol is a white amorphous powder soluble in a mixture of alcohol and ether and melting at 275°.

Amber was formerly much esteemed in medicine; but it is now used chiefly as an ornament, sometimes for photographic and fine varnishes, and in the manufacture of artificial silk.

Ambrite. The lignite formation in Auckland, New Zealand, furnishes this resin in large lumps. It is brittle, semi-transparent, and of a yellowish-grey colour. Its sp.gr. is 1·034, and its hardness 2. It is insoluble in most solvents, but dissolves partly in carbon disulphide. It contains 0·59 p.c. moisture and 0·18 p.c. ash. The dried ash-free resin contains C 80·95 p.c.; H 9·87 p.c.; O 9·18 p.c. (Bedson, Trans. Fed. Inst. Mining Eng. 16, 338).

Anthracoxene. This resin is found between the coal strata near Schlau in Bohemia. When seen in masses it is brownish-black in colour, but in thin layers is hyacinth red. It is brittle and swells when heated. According to Laurentz anthracoxene is a mixture of several resins (Sitz. Ber. K. Akad. Wien. 21, 271; J. pr. Chem. [i.] 69, 428).

Asphalt. This substance, found in various parts of the world, is probably the result of the decomposition of vegetable matter, and is closely allied to petroleum. *V.* Asphalt.

Berengelite, Berengela resin. A bituminous resinous mineral found in Peru. It is used for caulking ships. It has a dark-brown colour and is soluble in alcohol or ether, and melts below 100° (Johnston, Phil. Mag. [iii.] 14, 87).

Boloretin. Derived from the fossil fir wood found in the Danish peat bogs. It is soluble in ether but not in cold alcohol, and melts at 75° to 79° (Forchhammer, Annalen, 41, 44; Krämer, Arch. Pharm. [ii.] 27, 73).

Brusterort Resin, Unripe amber. This fossil resin resembles krantzite and differs from amber in not containing succinic acid (Spirgatis, J. 1871, 1188; 1872, 1146).

Bucaramanga Resin. Boussingault examined this resin (Ann. Chim. Phys. [iii.] 6, 507). It comes from Bucaramanga in New Granada. In appearance it resembles amber, but it does not contain succinic acid.

Burmite. A semi-transparent resin found near Maingkhwan, in the Hukong valley (Helm, Records Geol. Survey India, 25, 180; 21, 6, 9; Schriften Ges. Danzig, 8, 63).

Cedarite, Chemawinite. An amber-like resin found on the shore of Cedar Lake near the mouth of the North Saskatchewan. It occurs as isolated grains rarely as large as a pea and never larger than a walnut (Harrington, Amer. J. Sci. 24, 332; Klebs, Jahrb. Min. 1898, ii. 212).

Copalin, Highgate resin. The blue clay of Highgate Hill contains roundish lumps of this fossil resin. It was studied by Johnston (Phil. Mag. [iii.] 14, 87) and Bastick (Pharm. J. 8, 339). It resembles copal.

Euosmite. An aromatic resin found in the lignite of Thumsenreuth in Bavaria. It consists of brownish yellow pulverulent masses or lumps.

Gedanite. A resin found with succinite on the Baltic coast. It closely resembles succinite but melts at a lower temperature, and contains less sulphur (Helm, Schriften Ges. Danzig, 4, No. 3, 214; Arch. Pharm. 233, 191; Tschirch and Aweng, *ibid.* 232, 660).

Glessite. A resin found with gedanite and succinite. It has characteristic spherical microscopic cell-like forms (Helm, Schriften Ges. Danzig, 5, No. 1–2, 291; Tschirch and Aweng, Arch. Pharm. 232, 660).

Guayaquillite. From Guayaquil in South America (Johnston, Phil. Mag. [iii.] 13, 329).

Hartin. A white, inodorous, and tasteless resin found in the lignite of Oberhart, Austria. It is said to have the composition $C_{10}H_{17}O$ (Schrötter, Pogg. Ann. 54, 45).

Hartite. Another resin found in the same place as hartin. According to Schrötter (*ibid.* 54, 45), it consists of a hydrocarbon of the formula C_3H_5. Hartite has also been investigated by Haidinger (*ibid.* 54, 261), and by Rumpf (J. pr. Chem. [i.] 107, 189).

Ixolite. Occurs together with hartite (Haidinger, Pogg. Ann. 56, 345).

Jaulingite. From Jauling in Austria (Ragsby, Sitz. Ber. K. Akad. Wien. 16, 366).

Krantzite. This is a variety of retinite (Bergemann, J. pr. Chem. [i.] 76, 65).

Middletonite. The coal seams near Leeds and at Newcastle contain this resin. It was analysed by Johnston (Phil. Mag. [iii.] 12, 261). Two similar fossil resins found in the coal measures were examined by Macadam (Chem. News, 59, 1).

Piauzite. An earthy resin examined by Haidinger (Pogg. Ann. 42, 275). Hardness 1·5, sp.gr. 1·22, and m.p. 315°.

Pyroretin. A brown resin from the lignite of Salesl, near Aussig in Bohemia (Stanek, Sitz. Ber. K. Akad. Wien. 12, 551).

Retin Asphalt. This is a yellow-brown earthy-looking resin, the sp.gr. of which varies from 1·07 to 1·35. That from the lignite of Bovey in Devonshire was examined by Hatchett (Phil. Trans. 1904, 404) and later by Johnston (*ibid.* 1840, 347). Johnston found it to consist of 13·23 p.c. mineral matter, 27·45 p.c. resin insoluble in alcohol and 59·23 p.c. resin soluble in alcohol. The resin soluble in alcohol gave the formula $C_{40}H_{54}O_6$, and was called by Johnston *retinic acid.* Other varieties of retin asphalt occur in the neighbourhood of Halle in Germany (Bucholz, Schw. J. 1, 290) and near Cape Sable in the United States.

Retinite, Walchovite. This resin, of which there are several varieties, occurs in the coal mines of Walchow in Moravia (Schrötter, Pogg. Ann. 59, 61; Cerutti, Arch. Pharm. [ii.] 22, 286). Retinite from Thessaly, *v.* Zengelis (Chem. Zentr. 1901, ii. 833).

Schleretinite. Obtained from the coal mines of Wigan (Mallet, Phil. Mag. [iv.] 4, 261).

Tasmanite. The aluminous rocks along the Mersey river in Tasmania yield small scales or plates of this resin. It contains sulphur, and, according to Church (Phil. Mag. [iv.] 28, 465), has the formula $C_{40}H_{62}O_2S$.

Val d' Arno Superiore Resin. This fossil resin, called by the peasantry 'terra che brucia,' closely resembles the Weissenfels resins. Alcohol separates it into *α-resin* $C_{40}H_{64}O_8$, melting at 75°–90°, and *β-resin* $C_{40}H_{58}O_5$, which melts above 120° (Guareschi, Cimento, 5, 175).

Xyloretin. A crystalline resin having the formula $C_{10}H_{16}O$ found in the fossil pine trunks of the Danish peat-bogs. It is insoluble in water, soluble in alcohol, and melts at 165°. Heated with potassium it gives a metallic derivative, with liberation of hydrogen (Forchhammer, Annalen, 41, 42; Schrötter, Pogg. Ann. 59, 54).

Resins of Weissenfels Lignite. A series of resinous substances have been isolated from the products of distillation of this lignite. They have been investigated by Brückner (J. pr. Chem. [i.] 57, 1) and Wackenroder (Arch. Pharm. [ii.] 60, 23). For other fossil resins, *v.* Dana Mineralogy, 6th ed., 1002.

Guaiacum Resin. *Resina guaiaci.* (*Résine de Gaïac,* Fr.; *Guaiakharz,* Ger.). Two West Indian species of guaiacum tree, *G. officinale* (Linn.) and *G. sanctum* (Linn.), yield the resin, Flück. a. Hanb. 100; Bentl. a. Trim. 41). It is obtained partly as a natural exudation, partly by means of incisions, and in some places the trees are cut down and the trunks set on fire at each end, when the warm resin exudes freely from incisions made in the middle. In commerce guaiacum resin appears in 'tears' or in masses. It is brittle, and, although at first of a reddish colour, becomes greenish by superficial oxidation (*v.* Schiff, Annalen, 111, 372). It has a faint balsamic odour, although it contains no benzoic or cinnamic acid. The sp.gr. is 1·20 and it melts at 85°, when the balsamic odour is more marked. The resin is soluble in alcohol, ether, acetone, chloroform, and in caustic alkalis; but in benzene or carbon disulphide it only dissolves partially. Solution of guaiacum resin in alcohol is a very sensitive reagent for oxidising agents. Ferric chloride, for instance, strikes with such a solution a dark-blue colour. Reducing agents discharge the colour, which reappears on oxidation (*v.* Schönbein, Zeitsch. anal. Chem. 8, 67; J. pr. Chem. [i.] 102, 164; Schaer, Zeitsch. anal. Chem. 9, 430; Schönn, *ibid.* 9, 210). According to Kowalewsky (Chem. Zentr. 1889, 210), the action of ozone on the resin gives rise, not simply to a blue-coloured product, but to a series of colours of which blue is about the middle member. This observer notices that the presence of moisture is necessary, ozone giving no colour with dry guaiacum (*v.* Hager, Zeitsch. anal. Chem. 26, 261). The solution is not coloured blue by hydrogen peroxide, a reaction which serves to distinguish that compound from ozone.

In presence of such a substance as blood, however, the blue colour appears. If a spot of blood be moistened with freshly prepared alcoholic solution of the inner unoxidised portions of guaiacum resin, and then with an ethereal solution of hydrogen peroxide, a blue colour is produced which can often be made more evident by transference to white blotting paper. This property of guaiacum is occasionally resorted to as a *means of identifying blood stains*. Further investigations have been made on the nature and formation of guaiacum blue by Doebner (Arch. Pharm. 234, 614); Schaer (Verh. Natur. Ges. Basel, 13, 287); Petit and Mayer (Compt. rend. 141, 193); Neumann-Wender (Chem. Zentr. 1905, i. 122); Carlson (Zeitsch. physiol. Chem. 55, 260). For methods of testing guaiacum resin, *v.* Hager (Zeitsch. anal. Chem. 26, 261), and for detection of colophony, Hirschsohn (*ibid.* 37, 459).

Crude guaiacum resin heated with an alcoholic solution of caustic potash yields a salt of *guaiaretic acid* $C_{20}H_{26}O_4$, which falls to the bottom of the vessel in a crystalline form (Unverdorben, Pogg. Ann. 16, 369). The free acid constitutes 10 p.c. of guaiacum resin. It is insoluble in water, but is soluble in alcohol, ether, and most solvents. It melts at 86°. Guaiaretic acid is not coloured blue by oxidising agents. It yields a diacetyl and a benzoyl derivative (Herzig and Schiff, Ber. 30, 378; Monatsh. 18, 714). If the alcoholic mother-liquor from the potassium guaiaretate be treated with hydrochloric acid a heavy amorphous precipitate falls, which after washing, yields to ether the α-resin or *guaiaconic acid*. This constitutes 70 p.c. of the crude resin. It was isolated by Hadelich (J. pr. Chem. [i.] 87, 321), and also studied by Doebner and Lücker (Arch. Pharm. 234, 590). After treatment of the hydrochloric acid precipitate with ether, there remains a residue amounting to about 10 p.c. of the original resin. This is the *β-resin*. It is soluble in alcohol and acetic acid, but insoluble in ether, benzene, chloroform, and carbon disulphide. Besides a little gum and mineral matter two other constituents have been found in small quantity in guaiacum. One of these is *guaiacic acid* $C_{12}H_{16}O_6$, which occurs only in traces in the resin but in much larger proportion in guaiacum wood (Thierry, J. Pharm. Chim. 27, 381). It forms colourless needles which sublime unchanged and are soluble in water and alcohol. The other substance is a colouring matter *guaiacum yellow*, first noticed by Pelletier and obtained by Hadelich in pale yellow octahedral crystals, $C_{20}H_{20}O_7$, m.p. 115° (D. and L.). It is a weak acid, and dissolves in sulphuric acid with a transient blue colour.

Guaiaconic acid was isolated from guaiacum resin by Richter (Arch. Pharm. 244, 90), who extracted the resin with boiling benzene and precipitated the concentrated extract with light petroleum. The precipitate was then extracted with ether to which chloroform was added as the extraction progressed: this extract was then added to light petroleum which precipitated the guaiaconic acid. This was dissolved in benzene from which solution *β-guaiaconic acid*, $C_{21}H_{26}O_5$, crystallised in small rhombohedra. It melts at 127°, forms a dibenzyol derivative, m.p. 138°, is insoluble in aqueous alkali hydroxides and is not changed to blue by oxidising agents. The benzene mother-liquor contained *α- guaiaconic acid* $C_{22}H_{26}O_6$, or $C_{22}H_{24}O_6$, which was obtained as a light powder by evaporating the mother-liquor and dissolving the residue in a mixture of ether and chloroform and precipitating by pouring into light petroleum. It melts at 73°, forming a green liquid which becomes brown at 101°, forms a tribenzoyl derivative, m.p. 133°–135°, and is insoluble in aqueous alkalis. Under the influence of oxidising agents, or exposed to the air, α-guaiaconic acid changes to a blue substance.

The products of the destructive distillation of guaiacum are very interesting. The lighter portions contain *guaiacene*, *guaiol*, or *tiglic aldehyde* $CH_3{\cdot}CH{:}C(CH_3)COH$ (Deville, Compt. rend. 17, 1143; 19, 134; Volckel, Annalen, 89, 346). Among the heavier products are guaiacol creosol and pyroguaiacin. *Guaiacol*

$$C_6H_4(OCH_3)OH[1{:}2]$$

is the monomethyl ether of orthodihydroxybenzene or catechol. This aromatic oil, which boils at 200°, is readily prepared from catechol and potassium methyl sulphate (Gorup, *ibid.* 147, 248). *Creosol* $C_6H_3(CH_3)(OCH_3)OH[1{:}3{:}4]$ is the monomethyl ether of homocatechol (Hlasiwetz, Annalen, 106, 339). It is a faintly aromatic smelling oil, which boils at 220°, and may be prepared by distilling homovanillic acid with lime (Tiemann and Nagai, Ber. 10, 206). *Pyroguaiacin* condenses towards the close of the distillation in pearly crystals. It was investigated by Pelletier and Deville (Compt. rend. 17, 1143), Ebermayer (J. pr. Chem. [i.] 112, 291), Nachlauer (Annalen, 106, 382) and Hlasiwetz (*ibid.* 106, 381; 112, 182). According to Wieser (Monatsh. 1, 595), it has the formula $C_{18}H_{18}O_3$, whilst Herzig and Schiff (*ibid.* 19, 95) give $C_{13}H_{14}O_2$. The crystals melt at 180·5°, boil at 258° (80–90 mm.), are nearly insoluble in water and alcohol, and only sparingly soluble in ether. When pyroguaiacin is distilled with zinc-dust it yields the hydrocarbon *guaiene* $C_{12}H_{12}$ in the form of brilliant plates which melt at 97°–98° and possess a faint blue fluorescence. Wieser obtained two other compounds from pyroguaiacin: the one by oxidation in acetic acid solution, which gave *guaiene-quinone*, having the formula $C_{12}H_{10}O_2$; and the other by fusion with caustic potash, which yielded a compound m.p. 202°, and has probably the formula $C_{12}H_{12}O_2$. When guaiacum itself is melted with potash, protocatechuic acid is found among the products (Bötsch, Monatsh. 1, 615).

By distilling guaiacum resin under reduced pressure, Richter (Arch. Pharm. 244, 90) obtained tiglic aldehyde, guaiacol, creosol, pyroguaiacin, and a substance which boiled at 255°–260° (4 mm.), resinous in character at first but yielding crystals by the slow evaporation of its solution in benzene and light petroleum. This melts at 107°, has the composition $C_{19}H_{20}O_5$, and forms a dibenzoyl derivative melting at 143°. Guaiaretic acid on distillation yields tiglic aldehyde, guaiacol and pyroguaiacin (Doebner and Lücker); Herzog and Schiff, however, were unable to detect tiglic aldehyde. Guaiaconic acid also yields these three compounds on distillation under ordinary pressure (D. and L.). Under reduced pressure, the acid yielded tiglic aldehyde, guaiacol, and other substances, the formation of which seems to depend on the rate of distillation (Richter).

Guaiacum is used in medicine as an alterative in gout, rheumatism, and syphilis.

Hemlock Spruce Resin. *Canada Pitch; Pix Canadensis* (*Poix de Canada*, Fr.; *Canadisches Pech*, Ger.). The hemlock spruce, *Tsuga canadensis* (Carr.), yields a reddish-brown resin nearly allied to Burgundy pitch, *v.* OLEORESINS.

Indian Hemp Resin (*Cannabin*). The common hemp, *Cannabis sativa* (Linn.), when grown in India develops a physiological activity not different in kind, but of greatly increased intensity, to that possessed by the plant in Europe or America. For drawings *v.* Bentl a. Trim. 231. Indian Hemp (*Cannabis Indica*, Brit. Pharm.; *Chanvre indien*, Fr.; *Indischer Hanf*, Ger.) contains, together with a *volatile oil*, a resin to which the name *cannabin* has been applied, and to which the powerful narcotic properties of the drug are ascribed (Roux, J. Pharm. Chim. Feb. 1887). This resin was isolated by T. and H. Smith (Pharm. J. 6, 171) as a brown amorphous solid. The method employed for its extraction was essentially treatment of the dry aqueous extract of the herb with alcohol, purification of the alcoholic solution, and precipitation of the resin therefrom by water. Cannabin so obtained possesses narcotic properties in a very high degree.

'Charas,' which consists essentially of the resinous exudation from the stems, leaves, and flower heads of the unfertilised female plant and which is considered by the Indian natives to be the most potent preparation of Indian hemp, has been investigated by Wood, Spivey, and Easterfield (Chem. Soc. Trans. 69, 539). These inquirers have isolated a terpene $C_{10}H_{16}$; a sesquiterpene $C_{15}H_{24}$, identical with the oil isolated by Valenta (Gazz. chim. ital. 10, 540), and afterwards by Vignolo (*ibid.* 25, i. 110) from cannabene, the oil which Personne (J. Pharm. Chim. [iii.] 31, 46) obtained by distilling the hemp plant with water; a paraffin, probably $C_{29}H_{60}$; and a red oil, *cannabinol*, to which the highly characteristic physiological effect of Indian hemp is due. In a further paper (Chem. Soc. Trans. 75, 20), this oil is shown to be a mixture of a compound $C_{21}H_{26}O_2$, for which the name cannabinol is retained, with one or more substances having a lower percentage of carbon. Cannabinol boils at 285° (8 mm.), coming over as an almost colourless oil which on cooling solidifies as a transparent resin. It yields an acetyl derivative, $C_{21}H_{25}O_2{\cdot}CO{\cdot}CH_3$, m.p. 75°. On treatment with cold fuming nitric acid, a trinitro derivative $C_{21}H_{23}(NO_2)_3O_2$ is obtained, crystallising in the form of bright yellow plates, which, when quickly heated, melt at 160° with some decomposition. This compound, on oxidation with hot nitric acid, gives *nitrocannabinolactone* $C_{11}H_{11}NO_4$, identical with the *oxycannabin* of Bolas and Francis (Chem. News, 24, 217) and of Dunstan and Henry (Chem. Soc. Proc. 1898, 44), together with normal butyric, valeric, and other fatty acids. Nitrocannabino lactone crystallises in faintly yellowish needles, melting at 178° (*v.* also Czerkis, Annalen, 351, 467).

Among other constituents occurring in small quantities in Indian hemp, nicotine was found by Preobraschensky (Pharm. Zeit. 1876, 705), but its presence is denied by Siebold and Bradbury (Pharm. J. [iii.] 12, 326). The latter, however, find traces of a new volatile alkaloid *cannabinine*, and a similar base has been isolated by H. F. Smith (*ibid.* [iii.] 22, 267). Another alkaloid *tetanocannabine*, according to Hay (*ibid.* [iii.] 13, 998), exists in the herb; but this is questioned by Warden and Waddell (*ibid.* [iii.] 15, 574). Tetanocannabine is possibly identical with choline, found by Jahns (Arch. Pharm. 25, 479) to be a constituent of Indian hemp.

Jalap Resins. The *true jalap resin* is extracted from the roots of *Ipomœa Purga* (Hayne) by alcohol, and, after concentration of the alcoholic solution, precipitated therefrom by water.

Jalap resin has generally been assumed by investigators to be a mixture of two amorphous glucosidic constituents; one soluble in ether, *jalapin*, and the other insoluble in ether, *convolvulin*. For a record of the work on these substances, *v.* Tschirch (Die Harze, Bd. 11, Leipzig, 1906). Power and Rogerson (J. Amer. Chem. Soc. 32, 80) have shown that jalap resin is much more complex than had been supposed, that its physiologically active components are all indefinite and amorphous, as are also the most important products of their hydrolysis and that consequently there is no justification for assigning empirical formulæ to these substances. The resin yielded 1·9 p.c. to light petroleum. This extract was physiologically inactive, contained cetyl alcohol and a number of fatty acids; also a *phytosterol* $C_{27}H_{46}O$, m.p. 134°–135°, and a *substance* $C_{18}H_{36}O$, m.p. 56°–57°, which gave the phytosterol reaction. The ethereal extract amounted to 9·7 p.c. of the resin; it was purgative and contained a small amount of *ipurganol*

$$C_{21}H_{32}O_2(OH)_2,$$

colourless needles, m.p. 222°–225°. It gave the colour reactions of the phytosterols. The residue of the ethereal extract after hydrolysis gave a little phytosterol, cetyl alcohol, volatile acids and amorphous products. The chloroformic extract amounted to 24·1 p.c. of the resin and was purgative. It yielded a little β-methylaesculetin, and after hydrolysis, formic, butyric *d*-α-methylbutyric acids, convolvulinic acid $C_{15}H_{30}O_3$, and possibly a higher homologue of the latter. Some dextrose was also formed so that a portion of the extract was glucosidic. The ethyl acetate extract, which was also purgative, formed 22 p.c. of the resin and on hydrolysis yielded products similar to those of the ethereal extract. The alcoholic extract amounted to 38·8 p.c. of the resin and was purgative. It was an almost white powder, m.p. 150°–160°, and gave, on hydrolysis, formic, butyric, and α-methyl butyric acids and also an amorphous product of complex composition.

Besides *Ipomœa Purga* (Hayne), which yields the true jalap resin, there are many other species of the genus *Ipomœa* which possess purgative properties, and a number of these plants, or the resins obtained from them have been employed in medicine (Power and Rogerson, Amer. J. Pharm. 80, 251; 82, 355; Chem. Soc. Trans. 101, 1).

Japanese Lacquer (*Urushi*). Urushi is the milky secretion of *Rhus vernicifera* (DC.) and is the material for the well-known Japanese lacquer varnish.

Ki-urushi (raw lacquer) is collected in June by making shallow cuttings in the stem of the tree when it exudes as drops from between the outer and inner barks. *Seshime-urushi* is an inferior kind of juice which exudes when branches and twigs of the tree have been immersed in water for some months and afterwards heated. The juice, when sent to the market, is usually mixed with more or less 'Mokuyiki,' a substance somewhat resembling urushi. Pure and unaltered urushi is a thick greyish fluid of dextrinous consistence which, under the microscope, is found to consist of minute globules, some of darker, others of lighter colour, mixed with small particles of opaque brownish matter. If the juice be exposed to moist air in a thin layer it dries to a lustrous translucent varnish. According to Yoshida (Chem. Soc. Trans. 43, 472), it contains urushic acid, gum, water, and a peculiar diastatic matter, also a very small proportion of a volatile poisonous body. The phenomenon of drying is due to the oxidation of urushic acid $C_{14}H_{18}O_2$ into oxyurushic acid, which takes place by the aid of the diastatic matter in the presence of oxygen and moisture.

Urushic acid or urushiol, purified by distilling in a high vacuum, is a viscid brown oil. Its composition agrees with the formula $C_{20}H_{30}O_2$. It yields a dimethyl ether and a diacetyl compound and behaves in general as a dihydroxyphenol. Dry distillation gives a mixture of hydrocarbons, catechol and small quantities of fatty acids and carbon dioxide (Majima and Chō, Ber. 40, 4390; Miyama, J. Coll. Eng. Tokyo, 4, 89; Majima, Ber. 42, 1418, 3664).

The poison contained in the lacquer is shown by Tschirch and Stevens (Arch. Pharm. 243, 504) not to be volatile but to consist of an oily substance soluble in light petroleum. It produces local dermatitis.

Kamala Resins. Kamala, a fine mobile powder of a dull-red colour, consists of the glands and hairs of the capsules of *Mallotus philippinensis* (Müller, Arg.). The shrub is described by Bentl. a. Trim. 236. Kamala has long been known as an orange dye-stuff, and more recently as a remedy for the expulsion of tape worm. Kamala, or a drug closely resembling it, is mentioned as early as the tenth century by the Arabian writers. It grows in Abyssinia, Arabia, the East Indies, and Australia. Good kamala yields at least three-quarters of its weight of resin, but it is often largely contaminated with mineral matter. According to Anderson (N. Ed. P. J. 1, 300; J. 1855, 669), who examined kamala in 1855, it contains: resinous colouring matter, 78·19 p.c.; albuminoids, 7·34 p.c.; cellulose, 7·14 p.c.; water, 3·49 p.c.; and ash, 3·84 p.c. *V.* Kirkby (Pharm. J. [iii.] 14, 897).

Anderson isolated from kamala a crystalline compound *rottlerin*, $C_{11}H_{10}O_3$, a wax, and a resin melting below 100°. Leube (J. 1860, 562), however, was unable to obtain any crystalline product, but the existence of rottlerin has been confirmed by A. G. and W. H. Perkin (Ber. 19, 3109) and Jawein (*ibid.* 20, 182). A further examination of kamala by A. G. Perkin (Chem. Soc. Trans. 63, 975; 67, 230) shows that it contains six distinct substances. Five of these, rottlerin, *iso*rottlerin, a wax, and two resins, one of high and the other of low melting-point, form the principal constituents, but there is also present a small quantity of a yellow crystalline colouring matter. Rottlerin crystallises in thin salmon coloured plates, m.p. 191°–191·5° (Perkin), 200°–201° (Bartolotti, Gazz. chim. ital. 24, i. 1), 203°–204° (Telle, Arch. Pharm. 244, 441). It has the molecular formula

$$C_{33}H_{30}O_9.$$

It yields a hexa-acetyl derivative and also metallic derivatives. The resin of low melting-point has the composition represented by $C_{12}H_{12}O_3$ and resembles rottlerin, with which it is evidently closely allied in most of its properties. The yellow colouring matter, *homorottlerin*, forms a beautiful glistening mass of yellow needles which melt at 192°–193°. It has the composition $C_{33}H_{36}O_9$ and is possibly a reduction product of rottlerin. The wax is a colourless, apparently crystalline mass, melting at 82°. Iso-*Rottlerin* crystallises in groups of minute plates melting at 198°–199° and in its appearance greatly resembles rottlerin, from which, however, it is readily distinguished by its behaviour towards solvents. The resin of high melting-point is a pale yellow amorphous substance of the formula $C_{13}H_{12}O_4$, closely allied to rottlerin in many of its properties. Kamala also contains a small quantity of a sugar which is extracted from it by water. For substitutes for kamala *v. Wars* or *Waras resin.*

Kosin Resin (*Koussin*). The female flowers of *Hagenia abyssinica* (J. F. Gmel.), a tree which grows in the higher districts of Abyssinia, contain a crystalline resin, *kosin.* Wittstein (Rep. Pharm. 71, 25) examined koso in 1840, and found the flowers to contain 6 p.c. of an acrid bitter resin, together with wax, gum, and one-fourth of their weight of tannin. Kosin was further studied by Pavesi (J. 1859, 585) and by Bedall (J. 1862, 513). To obtain it the drug is mixed with lime, and extracted first with alcohol and afterwards with water. The solutions are mixed together and concentrated. Acetic acid is then added, which liberates the kosin from its soluble calcium salt, when it slowly precipitates.

Commercial kosin was examined by Flückiger and Buri (J. 1874, 900; Flück. a. Hanb. 258), who found it to consist essentially of yellow rhombic crystals, which melt at 142°. The crystals are insoluble in water, but easily soluble in alcohol, ether, benzene, glacial acetic acid and in alkalis. Ferric chloride gives a red colour with an alcoholic solution of kosin. By repeated crystallisation from alcohol, these crystals have been separated into two compounds, *α-kosin*, melting at 160° and a little *β-kosin*, more soluble in alcohol and melting at 120°. Both have the composition

$$C_{21}H_{24}O_5(OMe)_2 \text{ or } C_{20}H_{20}O_5(OMe)_2$$

(Boehm and Lobeck, Arch. Pharm. 239, 672; *cf.* Daccomo and Malagnini L'Orosi, 20, 361). Various other compounds have been obtained from extracts of koso flowers. Leichsenring (Arch. Pharm. 232, 50) isolated *protokosin* $C_{29}H_{38}O_9$, long colourless shining needles, melting at 176°. Protokosin is without physiological action, and the poisonous character of the original drug has been traced to the presence of *kosotoxin* $C_{26}H_{34}O_{10}$, a pale yellow powder (*cf.* Kondakoff and Schatz, Arch. Pharm. 237, 493). Boehm and Lobeck found in a commercial ethereal extract of the flowers a small proportion of *anhydroprotokosin* $C_{58}H_{74}O_{17}$, m.p. 182°. This, when crystallised from alcohol containing a little water, is converted into Leichsenring's protokosin. Also small quantities of *kosidin* $C_{31}H_{46}O_{11}$, melting at 178°, were obtained. The main constituent, however, was kosotoxin, which melted at 62°. When heated with aqueous sodium hydroxide and zinc dust, kosotoxin is, to a large extent, converted into kosin, and the latter compound is also formed when kosotoxin is boiled with barium hydroxide.

Kosin is employed in medicine as a vermifuge.

Lac Resin. *Gum Lac; Lacca.* (*Laque*, Fr.; *Lack*, Ger.). Lac is an exudation produced by the puncture of the hemipterous insect, *Coccus lacca* (Kerr), on the young branches of many East Indian lacticiferous trees. The resin exudes and dries on the branch, covering it and imbedding the insects and protecting their eggs. The female insect contains a red colouring matter. The small branches covered with resin are known in commerce as *stick lac.* When the resin is removed it is called *seed* or *grain lac*, and when melted by boiling with water and cooled in thin layers it becomes *shellac.* The water in which seed or stick lac has been boiled contains the colouring matter, which on evaporation constitutes *lac dye.* Shellac is bleached by treatment with sulphurous acid or chlorine. It is soluble in alcohol, alkalis, and in hydrochloric and acetic acids. It consists of a mixture of resins, together with small quantities of wax, fat, and extractive matter (von Esenbeck and Marquart, Annalen, 13, 286; Benedikt and Ehrlich, Monatsh. 9, 158; Benedikt and Ulzer, *ibid.* 9, 580; Gascard, J. Pharm. Chim. [v.] 27, 365). It is used for varnishes, and is the basis of the better kinds of sealing-wax. A liquid shellac is prepared by the action of hot alkalis. (B. and E.)

Lac dye was examined by Schmidt (Ber. 20, 1287), who finds it to contain a crystalline compound *laccaic acid*, $C_{16}H_{12}O_8$ (?), the salts of which possess the characteristic red colour of the dye. The acid resembles carminic acid.

The purified resin of stick lac on hydrolysis yields *aleuritic acid* $C_{13}H_{26}O_4$, m.p. 101·5°, and a sticky substance which is probably a resinotannol (Tschirch and Farner, Arch. Pharm. 237, 35). These investigators also obtained from the colouring matter a substance *erythrolaccin* $C_{15}H_{10}O_5,H_2O$, which appears to be a hydroxymethyl anthraquinone. For the detection and estimation of rosin in shellac, *v.* Langmuir (J. Soc. Chem. Ind. 24, 12).

Lanoresin. A resin or gum-resin obtained from the washings of wool (J. Soc. Chem. Ind. 1890, 1046).

Masopin Resin. A resinous substance obtained from the Dschilte tree, and used in Mexico for chewing. It is a snow-white powder, without taste or smell, insoluble in water but soluble in alcohol or ether. From an ethereal solution crystals may be obtained. These melt at 155°, but in melting undergo a change by which the melting-point falls to 70°. Masopin has the composition $C_{22}H_{36}O$ (Genth, Annalen, 46, 124).

Mastich Resin. *Mastiche.* (*Mastic*, Fr.; *Mastig*, Ger.). Mastich is the concrete resinous exudation of *Pistacia Lentiscus* (Linn.), an evergreen shrub inhabiting the shores of the Mediterranean (Bentl. a. Trim. 242). It comes chiefly from the island of Scio. Mastich has been known from ancient times, but it is employed less and less in pharmacy, and is being replaced by other resins in the manufacture of the finer varnishes. It occurs in 'tears,' or in masses of a pale-yellow colour; is brittle, and has a faint balsamic odour. It softens in the mouth, and melts at about 108°.

Earlier investigations of the resin have been made by Johnson (Phil. Trans. 1839, 132) and Hartsen (Ber. 9, 316). A sample examined by Tschirch and Reutter (Arch. Pharm. 242, 104) was found to contain *a-* and *β-masticic acids* $C_{23}H_{36}O_4$, separated from the ethereal solution by 1 p.c. aqueous ammonium carbonate. 1 p.c. aqueous sodium carbonate then extracts *masticolic acid* $C_{23}H_{36}O_4$, crystals, m.p. 201°, and *a-* and *β-masticonic acids* $C_{32}H_{48}O_4$, melting at 96°–96·5° and 91°–92° respectively. The residue consists of *masticoresenes* with about 2 p.c. of essential oil (*cf.* Flückiger, Arch. Pharm. [iii.] 19, 170). A bitter substance is also present. A table showing the acidity, ether, and saponification numbers of several varieties of mastic is given by Dieterich (Pharm. Centh. 40, 453) and the solubility of the resin in different solvents by Coffignier (Bull. Soc. chim. [iii.] 27, 549).

Maynas Resin (*Calaba, Galba*). A resin extracted by incision from the tree *Calophyllum Calaba* (Jacq.) which inhabits the plains of San Martino and the Orinoco. When purified by solution in alcohol it crystallises in prisms. It is soluble in alcohol, ether, alkalis, and in acetic and sulphuric acids. Analysis led to the formula $C_{14}H_{18}O_4$ (Lewy, Ann. Chim. Phys. [iii.] 10, 380).

Mezereon Resin. The acrid constituent of mezereon bark is a resin. The bark is obtained from the shrubs of *Daphne Mezereum* (Linn.) and other species of *Daphne.* These shrubs, with their red, fragrant flower-clusters preceding the leaves, inhabit southern and middle Europe, and grow in England as far north as Yorkshire (*v.* Bentl. a. Trim. 225–227).

Mezereon *resin* has not been recently examined. It was prepared by Gmelin (Schw. J. 35, 11), and according to Zwenger (Annalen, 115, 17), it yields, on distillation, umbelliferone. Vauquelin (Ann. Chim. Phys. 84, 174), also Gmelin and Baer (Schw. J. 35, 1), isolated from various species of daphne a crystallisable compound *daphnin.* This was shown to be a glucoside by Zwenger (Annalen, 115, 1). It breaks up by the action of acids into glucose and *daphnetin.* Daphnetin has been synthesised by Pechmann (Ber. 17, 929), also Gattermann and Hobner (*ibid.* 32, 287). Among the other constituents of mezereon is a *vesicating fatty oil*, which occurs chiefly in the fruit (Martius, Arch. Pharm. [ii.] 110, 39).

In medicine mezereon is employed as an alterative in rheumatism and scrofula, and is sometimes used as a vesicant.

Norway Spruce Resin. *Burgundy Pitch; Pix*

Burgundica. (*Poix de Bourgogne*, Fr.; *Fichtentarr* or *Tannenharz*, Ger.). Burgundy pitch is the prepared resin of *Picea excelsa* (Link.) the Norway spruce fir. For drawing *v.* Bentl. and Trim. 261. The market is supplied with Burgundy pitch chiefly from the Grand Duchy of Baden, Austria, and Switzerland. The ordinary method of collection is to make incisions, and to allow the oleoresinous juice which exudes to harden on the trees. It is then removed and treated with boiling water, whereby a resin practically free from volatile oil is obtained. Burgundy pitch closely resembles colophony. It is employed in medicine for plasters. When colophony is melted and mixed with a little fat and water, and stirred as it cools until it solidifies, a mixture is obtained which has the opacity and other characters of Burgundy pitch, and is largely substituted for the true resin.

Palm-Wax Resin (*Ceroxylin*). Palm-wax, the product of *Ceroxylon andicolum* (Humb.), a palm of New Granada, contains a resin. It may be separated from the wax by solution in alcohol. It melts above 100°, and is said to have the composition $C_{20}H_{32}O$ (Boussingault, Ann. Chim. Phys. [iii.] 29, 330; 59, 19).

Pellitory Resin. The root of *Anacyclus Pyrethrum* (De Cand.), 'pellitory of Spain,' has long been known as a powerful local irritant and sialogogue. It comes for the most part from Algeria. A drawing of the plant is given by Bentl. and Trim. 151. The acrid properties of the root seem to depend upon its resinous constituent, *pyrethrin* (Gaultier and Parisol. J. Pharm. Chim. 1818, 49; 1834, 251; Köne, Ann. Chim. Phys. [ii.] 59, 328). Thompson (Pharm. J. [iii.] 17, 567) prepares the resin as follows: The root is powdered and percolated with alcohol. The residue is then acidified with acetic acid and extracted by boiling alcohol. Finally the two liquids are mixed together and evaporated. Thus obtained, pyrethrin is a mixture of an acid-brown resin with some, probably inactive, fixed oil. Pellitory contains, besides pyrethrin, fixed oil, gum, inulin, a trace of tannin, and, according to Buchheim (*ibid.* [iii.] 7, 315), a compound *pyrethrine*, analogous to piperine, which, by the action of caustic alkalis, takes up the elements of water and breaks up into *piperidine* and *pyrethric* acid (*cf.* Dunstan and Garnett, Chem. Soc. Trans. 67, 100). Pyrethrine forms white clustered needles, melts at 45° and has an extremely burning taste (Schneegans, Pharm. Zeit. 41, 668).

Similar resinous constituents are found in the root of German pellitory, *A. officinarum* (Hayne) (Bentl. and Trim. 152; Flück. and Hanb. 384).

Pepper Resin. Pepper appears in commerce as 'black,' 'white,' and 'long' pepper. The black and white varieties are the dried fruit of the same plant, the white appearance being due to the removal of the dark-coloured pericarp. Pepper is obtained from *Piper nigrum* (Linn.), a climbing shrub, indigenous to Travancore and Malabar, and cultivated largely in both the East and West Indies. Long pepper consists of the dried spikes of the minute fruits of *Piper Chaba* (Hunter), a shrub inhabiting the Indian Archipelago (*v.* Bentl. and Trim. 244–245). Pepper has been known from the earliest times. Theophrastus was acquainted with black and long pepper, and white pepper is mentioned by Dioscorides. The Romans levied duty on black pepper in Alexandria, A.D. 176 (Flück. and Hanb. 577).

The pungent taste of pepper is due to its *resin*, but this has not been studied chemically. Pepper contains 1 to 2 p.c. of a *volatile oil*, upon which its odour depends. The volatile oil was examined by Dumas (Annalen, 15, 159) and by Soubeiran and Capitaine (*ibid.* 34, 327). It consists essentially of a terpene boiling at 164° to 165°, and having the sp.gr. of 0·873 (Eberhardt, Arch. Pharm. [iii.] 25, 515). The most interesting constituent, however, is the crystalline alkaloid *piperine* $(C_5H_{10}N)C_{12}H_9O_3$, discovered by Oersted in 1819 (Schw. J. 29, 80). It was further investigated by Pelletier (Ann. Chim. Phys. [ii.] 16, 344; 51, 199) and others, and Stenhouse found it to be a constituent of cubebs (Annalen, 95, 106). Pepper contains from 5 to 15 p.c. of this compound. By the action of alcoholic potash it breaks up into the base *piperidine* $C_5H_{11}N$, and *piperic acid* $C_{12}H_{10}O_4$. Piperidine may be obtained, as Ladenburg has shown (Ber. 17, 513), by the action of nascent hydrogen on pyridine. An examination of pepper by Johnston (Chem. News, 58, 235; Analyst, 14, 41) has shown that piperidine exists ready formed in the spice to the extent of from 0·2 to 0·8 p.c. Pictet and Court (Ber. 40, 3771), however, by steam distillation of black pepper obtained a distillate which did not contain piperidine, but a base which is probably a C-methyl pyrroline, C_5H_9N. According to Buchheim, pepper contains another compound, *chavicin*, which by the action of alkalis yields *chavicic acid* and piperidin (Pharm. J. [iii.] 7, 315).

Pepper is used extensively as a spice. When ground it is liable to adulteration, chiefly with starch and serials. Such admixture is mostly detected by microscopical examination. See Blyth ('Foods: their Composition and Analysis'). For analysis of peppers of commerce *v.* Johnston (Analyst, 14, 41) (*v.* PEPPER).

Podophyllum Resin. *Resina podophylli* (*Resine de podophylle*, Fr.; *Podophyllumharz*, Ger.). This favourite purgative is obtained from the rhizome and rootlets of May apple, *Podophyllum peltatum* (Linn.), which, with its beautiful wax-like flower, grows abundantly throughout the American continent, east of the Mississippi and south of Hudson's Bay (Bentl. a. Trim. 17). It is also said to occur in Japan (Pharm. J. [iii.] 19, 346). Another species of the genus *Podophyllum*, which yields the Indian podophyllum, *P. Emodi* (Wallich), possesses the same properties as the American species. It inhabits the shady valleys of the Himalayas, and is abundant in Kunawin and Kashmir (Dymock and Hooper, Pharm. J. [iii.] 19, 585).

Besides the *resin*, upon which the purgative property of the drug depends, Mayer, who examined podophyllum in 1863 (Amer. J. Pharm. 1863, 97), reported it to contain berberine, saponin, and a colourless alkaloid; but no evidence of these compounds, at least in the crude resin, has been obtained by subsequent observers (Power, *ibid.* 1878, 369; Maisch, *ibid.* 1879, 590; Biddle, Pharm. J. [iii.] 10, 468).

The resin is prepared by extracting the dried and powdered drug with alcohol, and throwing the alcoholic solution into water or water acidified with hydrochloric acid, the latter helping the resin to agglomerate, and thus to subside more readily. The precipitate should be dried by simple exposure to the air, or, at all events, at temperatures below 35°. Thus prepared, podophyllum resin has a greyish-white, slightly yellow, or greenish-yellow colour. If higher temperatures be employed the resin is darker. A more distinct yellow colour is produced by the use of alum water as a precipitant. Variations in colour, observable in commercial specimens, have not been found to affect appreciably their physiological activity (Senier and Lowe, Pharm. J. [iii.] 8, 443; Klie, Amer. J. Pharm. 1887, 578; Busch, *ibid.* 1877, 548; Lloyd, Pharm. J. [3] 10, 70; Jones, Chem. Drug. 34, 701). The yield of resin varies from 3 to 5 p.c. From Indian podophyllum 12 p.c. of crude resin was obtained by Dymock and Hooper.

Podophyllum resin is soluble in alcohol and caustic alkalis. From its alkaline solution it is re-precipitated by acids. Although the resin is precipitated from its alcoholic solution by water, it is not insoluble in that menstruum. As much as 80 p.c. may be dissolved in hot water, and only a part of this re-precipitates on cooling. Power finds the crude resin to melt at 120° to 124°. Ether dissolves about 60 p.c. of the resin (*v.* Guareschi, Gazz. chim. ital. 10, 16).

The investigations of Podwyssotzki have thrown much new light on the chemistry of podophyllum (Arch. Path. u. Pharm. 13, 29; Pharm. Zeit. 20, 49, 140, 208, 777; Pharm. J. [iii.] 12, 217, 1011). The author reviews experimentally the literature of podophyllum, and isolates a series of definite crystalline and other constituents, the properties of which he has studied, and to one of which he finds the medicinal activity to be due. These compounds exist both in podophyllum and in the resin, but they are more readily obtained from the crude drug. The essential constituent is a colourless, amorphous, poisonous bitter substance, *podophyllotoxin*, which, by the action of lime-water, splits into a neutral, crystalline, bitter, poisonous compound, *picropodophyllin*, and the calcium salt of inactive *picropodophyllic acid*. The colour of podophyllum is due to the compound *podophylloquercetin*, which crystallises in yellow needles with a metallic lustre. The other constituents are inert *podophyllic acid* and an inactive *resin* insoluble in ether. The active purgative constituent is picropodophyllin.

To obtain podophyllotoxin podophyllum is extracted with cold chloroform, which must be free from alcohol, otherwise podophylloquercetin is dissolved also. The chloroform solution concentrated to a syrup is poured into ether, when inert podophyllic acid, insoluble in ether, is precipitated. If the clear liquid is now dropped into light petroleum this solvent retains the fat, and the podophyllotoxin is precipitated as a white powder. It may be purified by re-solution in chloroform and repetition of this process. Thus obtained, podophyllotoxin is a very bitter white or pale-yellow powder, and dissolves in weak spirit or in hot water. It is readily soluble in chloroform or ether, but it is insoluble in light petroleum.

Picropodophyllin is prepared from podophyllotoxin by mixing the alcoholic solution with slaked lime and evaporating to dryness on a water-bath. The residue extracted with hot absolute alcohol yields silky crystals of picropodophyllin on cooling. The resinous compound, picropodophyllic acid, may be prepared from the residue, after extraction of picropodophyllin, in which it exists in combination with calcium. It has no physiological activity, and was not obtained in a sufficiently pure state for analysis. After podophyllum has been treated with chloroform as described, and with light petroleum to remove fat, the podophylloquercetin, which is insoluble in these solvents, is extracted by ether. The ethereal solution is evaporated, and the podophylloquercetin purified by conversion into a lead compound, and subsequent regeneration and re-solution in ether. After removal of the ether it remains as a yellow powder, which may be obtained in yellow crystals by sublimation. On exposure to the air it changes to green, a fact which accounts for some of the colours observable in the commercial resin. It has no emetic or aperient action, but is, perhaps, the cause of the intestinal pain which sometimes accompanies the administration of podophyllum. Podophylloquercetin is the colouring agent of podophyllum. It is insoluble in water, and forms with alkalis bright yellow solutions. Ferric chloride colours it dark green.

Kürsten (Arch. Pharm. 229, 220), by a slightly modified process, has obtained the constituents discovered by the former chemist in a crystalline condition. He ascribed to podophyllotoxin the formula $C_{23}H_{24}O_9,2H_2O$ and showed that the picropodophyllin obtained from that compound by the action of alkalis is an isomeride, and concluded that the picropodophyllic acid of Podwyssotski is an oxidation product which can be prepared by the action of alkaline potassium permanganate.

Further work by Dunstan and Henry (Chem. Soc. Trans. 73, 209) has proved that the constituents of *P. emodi* (Wallich) are identical with those of *P. peltatum* (Linn.). Crystalline podophyllotoxin has the formula $C_{15}H_{14}O_6.2H_2O$ and melts at 117°. The anhydrous compound melts at 127°. When acted upon by aqueous alkalis it is converted into the isomeric picropodophyllin which melts at 227°. The acid produced at the same time is not an oxidation product as Kürsten supposed but the acid $C_{15}H_{16}O_7$, of which picropodophyllin is the anhydride. The yellow colouring matter is concluded to be identical with the quercetin of quercitron bark (*cf.* Kürsten).

The resin *podophyllo-resin* left after the removal of podophyllotoxin and podophylloquercetin from podophyllum resin is a dark coloured powder physiologically active. After purification it is obtained as a transparent reddish-brown substance softening and becoming semi-liquid a few degrees above the ordinary temperature. It yields a crystalline acetyl derivative and probably has the formula $C_{12}H_{12}O_4$. The physiological action of podophyllum is due partly to the podophyllotoxin it contains and partly to the podophyllo-resin. Picropodophyllin, picropodophyllic acid and the quercitrin have very little, if any, purgative action.

The rhizome of *P. emodi* (Wallich) contains from 10 to 12 p.c. of resin, whereas the American drug contains about 5 p.c.

Kremel (Pharm. Post, 1889, 105) suggests that podophyllum resin should be valued by a determination of the proportion of podophyllotoxin which it contains. About a gram of the resin is treated with chloroform in the cold as long as anything is dissolved; the solution obtained is evaporated to a small bulk, and then poured into twenty times its volume of light petroleum. The podophyllotoxin separates, and is collected, dried, and weighed. Commercial specimens of resin yield 20 to 30 p.c.

Rhubarb Resin (*v.* RHUBARB-ROOT).

Sandarac. *Sandaraca.* (*Sandaraque*, Fr.; *Sandarak*, Ger.) A pale yellow translucent exudate from a small evergreen tree, *Callitris quadrivalvis* (Ventenat), which inhabits north-western Africa. It somewhat resembles mastich, but is brittle between the teeth. The investigations of Unverdorben (Scher. J. 60, 82) and Johnston (Phil. Trans. 1839, 293) show that it contains three resins which can be separated by means of their different behaviour towards alcohol and alcoholic potash.

Balzer (Arch. Pharm. 234, 289) obtained two resin acids from sandarac, *sandaracolic acid*, m.p. 140°, and *callitrolic acid*, m.p. 248°.

Examined by Henry (Chem. Soc. Trans. 79, 1144), the essential oil of sandarac resin was found to contain a diterpene and *d*-pinene. Two resin acids were isolated, one *i*-pimaric acid $C_{20}H_{30}O_2$, m.p. 171°, is isomeric with the *d*-pimaric acid isolated by Vesterburg from Bordeaux colophony, but differs from the latter in being optically inactive. The other acid corresponds to Balzer's callitrolic acid and has the composition $C_{30}H_{48}O_5$.

Tschirch and Wolff (Arch. Pharm. 244, 684) have extracted amorphous *sandaracic acid* $C_{22}H_{34}O_3$, m.p. 186°–188° (decomp.), *sandaracinolic acid* $C_{24}H_{36}O_3$, decomposing at 265°–275°, and a small quantity of *sandaracopimaric acid* (Henry's *i*-pimaric acid). The non-volatile residue consisted of amorphous *sandaracoresen* $C_{22}H_{36}O_2$, m.p. 57°.

Australian sandarac or 'white pine resin' is almost entirely the natural exudation product of *Callitris calcarata* (R. Br.) and *C. glauca* (R. Br.) (Smith, J. Soc. Chem. Ind. 30, 1358). It differs from the common sandarac chiefly in the larger size of its 'tears,' the name given to the small hard masses of resin formed on the trees by the evaporation of a portion of the volatile matter. Henry (*l.c.*) found this resin to contain *d*-pinene and the two resin acids already obtained from common sandarac. Sandarac, which is also known in commerce as 'gum juniper,' is used in the preparation of varnishes.

Analytical constants of sandarac resin are given by Dieterich (Pharm. Centh. 40, 453) and its solubility in various solvents by Coffignier (Bull. Soc. chim. [iii.] 27, 549).

Tonquin Lac Tree. The sap of the Tonquin lac tree, *Rhus succedanea* (Linn.), which forms the basis of various kinds of lacquer is a thick, nearly white alkaline cream, superficially oxidisable by air to an intensely black impervious substance insoluble in the usual solvents. Complete oxidation only takes place in the presence of a diastatic ferment *laccase*, which can be separated from the other essential constituents of the sap by means of alcohol, in which it is insoluble. From the portion of the sap soluble in alcohol, a substance *laccol* can be precipitated by lead acetate. It is a thick oil, intensely irritating to the skin. It is readily oxidisable in the air to a reddish, viscous or resinous substance (Bertrand, Bull. Soc. chim. [iii.] 11, 717; Compt. rend. 120, 266).

Wars or **Waras Resin.** This drug, which, coming from India or Arabia, has from time to time appeared as a substitute for kamala, consists of the glands and hairs of species of *Flemingia.* The powder resembles kamala, but is of a darker colour. It yields resin to the same extent as kamala, and is closely related to that drug in all its characters. *V.* Flückiger (Pharm. J. [ii.] 9, 279; [iii.] 17, 1029; 18, 110), Kirkby (*ibid.* [3] 14, 897), Dyer (*ibid.* [iii.] 14, 917, 969) and Hooper (*ibid.* [iii.] 18, 213).

An investigation of waras by A. G. Perkin indicates that it contains five distinct substances, *flemingin, homoflemingin, resins of high and low melting-points*, and a *wax.* There is a close analogy between these compounds and the similar products obtained from kamala. Flemingin $C_{12}H_{12}O_3$, is a dull orange-red, crystalline powder melting at 171°–172°. Homoflemingin consists of pale yellow needles melting at 165°–166°. It has the same composition as flemingin (Chem. Soc. Trans. 73, 660). A. S.

RESINATE LAKES. These lakes are prepared by dissolving 100 parts of pale-coloured resin in a solution of 33 parts of soda crystals in 1000 parts of water. The mixture is boiled for an hour, after which it is cooled down to about 50° by the addition of 1000 parts of cold water, and then the filtered solutions of such basic dyes as magenta, methyl-violet, brilliant green, auramine, &c., are added. The amount of dye used depends on the depth of colour desired, and varies between 5 and 15 p.c. on the amount of resin. The resin-soap solution must be of the right temperature and degree of concentration when the addition of dye is made, so as to avoid the separation of the colour bases in the form of resinates. A slight excess of a dilute solution of a metallic salt is added; in the case of zinc sulphate, 55 parts dissolved in 1000 parts of water are used for the above quantities of resin, &c. The solutions of magnesium salts must be very dilute, since otherwise the lake becomes resinous on drying. The lakes which are not to be used in the paste form are thoroughly dried at a temperature of 40° to 50°, or 70° in the case of magnesium lakes. The dried lakes are of an exceedingly fine bright colour. They are not affected by air or moisture, and boiling water fails to extract colouring matter. Weak alkalis and acids are also without action, and strong solutions of hypochlorites act very slowly on them, provided that light is excluded; but, in presence of light, oxidising agents act rapidly. Their solubility in alcohol depends upon the nature of the combined metallic base; magnesium lakes dissolve easily, calcium and barium lakes fairly easily, aluminium and iron lakes only slightly. Benzene, ether, chloroform, light petroleum, and other solvents dissolve them easily. Some of the lakes—those of aluminium, for instance—are decomposed when their solutions are kept for a little time, the metallic base separating, but others, such as those of zinc and calcium, keep indefinitely. They resist light fairly well. Lakes made with brilliant green resist badly, but those coloured with auramine, methyl-violet, safranine, chrysoidine, and particularly rhodamine, resist very well. The colours bleach more easily when in combination with aluminium and chromium than with zinc and magnesium. The action of light renders the lakes insoluble in benzene, liberating the colour-base, which may be extracted with hot water. The solutions of the lakes form good varnishes, whose elasticity and power of endurance are increased by the addition of a little indiarubber or guttapercha. The following is an example of such a varnish: 30 parts of magnesium lake are dissolved in 80 parts of benzene and 20 parts of chloroform, and the solution obtained mixed with 150 parts of a clear solution of 1½ p.c. of indiarubber in chloroform and benzene (A. Müller-Jacobs, Dingl. poly. J. 273, 139; J. Soc. Chem. Ind. 8, 770).

RESIN OIL. *Resin spirit.* Common resin or colophony is a substance which is left in the stills after distillation of spirits of turpentine (*v.* RESINS). It is a well-known brittle, but fusible and inflammable, solid which is found in commerce of various colours, from pale yellow to black. It consists of a mixture of acids, the exact composition of which, notwithstanding numerous researches, remains unknown. It is, however, usually regarded as consisting chiefly of abietic acid. These acids form greasy salts with alkalis, and resin is commonly employed as an ingredient in soap, as well as in the manufacture of varnishes.

The lower grades of resin are submitted to distillation with the object of producing an oil, suitable for use as a lubricant, and a spirit which is used in varnish-making. The distillation is carried out in cast-iron stills of charging capacity varying between 3 and 10 tons, the usual size being about 5 tons. The head of the still is rounded and provided with flanges by which it can be bolted on to the body, which has a hemispherical bottom. The condensing worm is usually made of copper. A considerable quantity of gas is given off during the distillation, containing carbon monoxide and hydrocarbons. The most volatile portion of the distillate, boiling between 80° and 250°, constitutes resin spirit or essence of resin, and is followed by the oil, which distils only between 300° and 400°. The residue in the still is pitch or coke, according to the extent to which the heating is carried. From 1 ton of resin the yield amounts to ½ to 1 cwt. of spirit, and 17 cwts. of oil. Water containing a little acetic acid comes over throughout the distillation, and the crude oils have a milky appearance in consequence.

Resin *spirit* is chiefly used in varnish-making, and as an adulterant of spirit of turpentine. It is refined by agitation with caustic soda and redistillation, or by redistillation only. Crude resin *oil* is a strongly fluorescent viscid oil, about one-fourth of which dissolves in solution of soda, the insoluble part consisting of a hydrocarbon (above 360°). Resin oil has also the property of uniting with slaked lime to form a greasy mass which is used as a lubricant. It is employed chiefly in collieries, and appears to be suitable only for iron bearings. In order to prepare the grease a smooth cream of slaked lime and water is first prepared, and a small portion of the oil is mixed with this in the proportion of about 4 parts of oil to 3 parts slaked lime. The two soon unite, forming a greasy semi-solid mass, with which an additional quantity of oil is afterwards incorporated until the requisite consistence is obtained. The finished grease contains about 1 part of lime to 20–25 parts of oil. The fluorescent bloom of the crude oil can be removed by washing it first with soda lye, and then exposing it to air in shallow iron vessels (Kelbe's patent, Ber. 13, 215a). It is also stated that the bloom can be destroyed by treatment with dinitronaphthalene, with nitrobenzene, or with hydrogen peroxide. Purified resin oil is used to adulterate lubricating oils, and is also mixed sometimes with rape oil and with boiled linseed oil, and forms an ingredient in some printing inks. The resin oils are generally sold under the name 'pine oil' (*q.v.*), and are classified, according to quality, as soft, medium, and hard.

The composition of both the essence and the oil has been studied by many chemists. The former consists of a complex mixture of hydrocarbons and other volatile substances, of which, when distilled, resin spirit generally yields more than half its volume below 120°. The following constituents have been isolated: A pentine, C_5H_8 (b.p. 50°) (Couërbe, J. pr. Chem. 1839, 18, 165); *iso*butyl-aldehyde (Tilden, Ber. 13, 1604); *iso*butyric, caproic and other fatty acids, methyl alcohol (very small quantity, 50 grms. from 150 kilos.); a hydrocarbon, C_9H_{12} (b.p. about 160°), homologue of benzene; ordinary cymene and a new cymene (*m*-propyltoluene): *m*-*iso*butyltoluene (b.p. 186°–188°); parabutyl-toluene (b.p. 176°–178°) (Kelbe, Ber. 13, 888, 1157; Annalen, 210, 1; Ber. 14, 1240; *ibid.* 15, 308); dipentine, $C_{10}H_{16}$ (Tilden, *ibid.* 13, 1604) together with a relatively large proportion of a heptine, C_7H_{12} (103°–104°), which has been shown by Morris (Chem. Soc. Trans. 1882, 167) to be probably methyl-propyl-allene $CH_3{\cdot}CH{:}C{:}CH{\cdot}C_3H_7$. This liquid is characterised by giving a succession of colours (yellow, red, green, and deep blue) when agitated with strong sulphuric or hydrochloric acid. In the presence of air and water it forms a glycol, $C_7H_{12}(OH)_2$, which crystallises with one molecule of water in the form of long slender prisms, which are frequently to be seen in old samples of resin spirit.

Resin oil consists of a mixture of abietic acid $C_{19}H_{28}O_2$ (Easterfield and Bagley; Mach) or $C_{20}H_{30}O_2$ (Levy; Koritschoner; Fahrion; Vesterberg), *v.* ABIETIC ACID, and small quantities of phenols with a mixture of hydrocarbons $(C_{10}H_{16})_n$ (b.p. above 360°), including *abietene* ($C_{18}H_{28}$, b.p. about 250°) and *colophene*, which constitutes about three-fourths of the whole.

W. A. T.

RESOPHTHALIN. *Fluorescein v.* TRIPHENYL METHANE COLOURING MATTERS.

RESORCIN. *Resorcinol v.* PHENOL AND ITS HOMOLOGUES.

RESORCIN BLUE *v.* OXAZINE COLOURING MATTERS.

RESORCIN BROWN. The sodium salt of xylidin-azo-sulphanilic-azo-resorcin. A brown powder, soluble in water and sulphuric acid, forming brown solution. Dyes wool brown in an acid bath.

RESORCIN YELLOW *v.* Azo- colouring matters.

RESORCINOFORM is an amorphous currant red powder prepared by dissolving 110 grms. of resorcinol in about 100 grms. of formaldehyde solution. Sufficient hydrochloric acid is then added to cause precipitation, the mixture, which turns pink, being kept well stirred. It is then drained on a filter and dried at 25°. Resorcinoform is said to be an active antiseptic for medicinal use (Monteuil, J. Soc. Chem. Ind. 1909, 542).

RESORCINOLBENZEÏN *v.* Aurin.

α- and *β-* **RESORCYLIC ACIDS** *v.* Protocatechuic acid.

RESORUFIN *v.* Oxazine colouring matters.

RETENE or 8-Methyl-2-*iso*Propylphenanthrene $C_{18}H_{18}$ (Bucher, J. Amer. Chem. Soc. 1910, 32, 374; Lux, Monatsh. 1908, 29, 763; *ibid.* 1910, 31, 939; Ber. 1910, 43, 688), occurs in high boiling tar oils derived from resinous pine-wood, and forms a faintly yellow, glittering, crystalline powder, which melts to a yellow oil at 98·5°, b.p. 394°. It can be melted together with different oils, fats, and hydrocarbons, and raises or lowers their melting-point accordingly. It can also be obtained by distilling resin oil or abietene with sulphur. Retene reacts with sulphur, yielding a compound, m.p. 86° (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1247). When heated with hydrogen in the presence of nickel oxide, the dodecahydroretene $C_{18}H_{30}$, b.p. 336°, is first obtained, then the perhydroretene $C_{18}H_{32}$, b.p. 300°–315°, which is not identical with fichtellite as had been formerly supposed (Ipatieff, Ber. 1909, 42, 2092; Liebermann and Spiegel, *ibid.* 1889, 22, 779).

Bromo derivatives of retene and of retene quinone, m.p. 197°, have been obtained (Scheller and Heiduschka, Arch. Pharm. 1910, 248, 89).

The fossil resin of the coniferæ, as found in Switzerland, Bavaria, and Denmark, contains retene as its principal constituent. It appears, indeed, very probable that the hydrocarbon is in every case derived from the coniferæ; *v.* Ekstrand, Annalen, 1877, 185, 75; E. v. Boyen, J. Soc. Chem. Ind. 1888, 116.

Further literature on retene and its derivatives: Kelbe, Chem. Zentr. 1887, 1504; Ekstrand, Bull. Soc. chim. [ii.] 24, 55; Bamberger and Hooker, Ber. 1886, 18, 1024, 1750; Schweitzer, Annalen, 1891, 264, 193; Perrier, Compt. rend. 116, 1298; Valeur, *ibid.* 1898, 126, 1148; Wiedemann, Ann. Physik. 1895, [ii.] 56, 18; Bamberger and Grob, Ber. 1901, 34, 533; D. R. P. 151981; Hofmann, Metzler and Lecher, Ber. 1910, 43, 181.

RETIN ASPHALT *v.* Resins.

RETINIC ACID *v.* Resins.

RETINITE *v.* Resins.

REXITE. An explosive consisting of nitroglycerin, 6·5–8·5 parts; ammonium nitrate, 64–68 parts; sodium nitrate, 13–16 parts; trinitrotoluene, 6·5–8·5 parts; dry wood meal, 3–5 parts.

REXOTAN *v.* Synthetic drugs.

RHAMNETIN *v.* Persian-berries.

RHAMNINOSE *v.* Carbohydrates.

RHAMNOSE *v.* Carbohydrates.

RHATANY ROOT. The dried root of *Krameria triandra* (Ruiz et Pav.), Peruvian rhatany, or *K. tomentosa* (St. Hill.), Savanilla rhatany. The bark contains about 20 p.c. of a kind of tannin. Is a strong astringent. Other species of *Krameria* produce Para rhatany and Texas rhatany, which are substituted for the first two kinds. For rhatany red *v.* Grabowski, Annalen, 143, 274.

RHEADINE *v.* Vegeto-alkaloids.

RHEONINE *v.* Acridine dyestuffs.

RHEOTANNIC ACID *v.* Tannins.

RHEUMATIN. A preparation of quinine used as an anti-rheumatic. *V.* Salicylic acid and Synthetic drugs.

RHINANTHIN $C_{29}H_{52}O_{20}$. A glucoside found in the seeds of *Rhinanthus Crista-galli* (Linn.), or yellow rattle, and which gives rise to the violet colour occasionally found in rye bread (Ludwig, Zeitsch. Chem. [ii.] 5, 303; Arch. Pharm. [ii.] 142, 199). It has a nauseously bitter-sweet taste, and crystallises in prisms.

RHODEINE. A hydrocarbon $nC_{10}H_{16}$ obtained from rosewood oil (Gladstone, Chem. Soc. Trans. [ii.] 10, 3).

RHODEOSE *v.* Carbohydrates.

RHODINOL $C_{10}H_{20}O$,

$$Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMeCH_2{\cdot}CH_2OH$$

a primary alcohol, is the odorous constituent of otto or oil of roses. It is contained in Turkish and German rose oils, in *Pelargonium odoratissimum* and is also said to occur in the following essential oils: ginger grass, lemon, Turkish palmarosa and neroli (Erdmann and Huth, J. pr. Chem. 1897, 56, 27).

Preparation. The impure rhodinol obtained by fractionating geranium oil from *Pelargonium odoratissimum* is converted into the acetyl derivative by heating it with acetic anhydride for 8 hours at 140°–145°. The product is cooled, washed with aqueous alkali, then with pure water and distilled *in vacuo.* The acetyl ester distilling at 127°–132°, is then saponified by solution in alcohol and treatment with an equimolecular quantity of potash. It is now allowed to stand for an hour, after which the alcohol is distilled off under diminished pressure; the residue is washed with water, filtered and distilled *in vacuô*, the fraction coming over at 120°–125°, being collected (D. R. P. 80007; Monnet and Barbier, Compt. rend. 1893, 117, 1092). Rhodinol can also be prepared by treating rhodinyl phthalate with sodium chloride, hydrolysing the resulting sodium salt with an alkali and distilling the rhodinol formed in steam (Erdmann, J. pr. Chem. 1897, [ii.] 56, 1); or by treating ethyl rhodinate (obtained from synthetical geranic acid) with sodium ethoxide (Bouveault and Gourmand, Compt. rend. 1904, 138, 1699). In the latter case, the rhodinol formed is racemic, but is otherwise identical with the natural product.

Properties. Rhodinol is a colourless, oily liquid, b.p. 110·5–111°/10 mm., sp. gr. 0·8812 at 16°/4° (Erdmann, Ber. 1898, 31, 356), b.p. 126·5°/16 mm., sp. gr. 0·8956 at 0°/0° (Barbier, Compt. rend. 1893, 117, 177), sp. gr. 0·8731 at 0°/0° (Barbier and Bouveault, *ibid.* 1896, 529), α_D 2° 34′ at 17°. It is an isomeride of licareol and geraniol, but it has also been regarded as identical with the latter and with *l*-citronellol (Bertram and Gildemeister, J. pr. Chem. [ii.] 49, 285; *ibid.* 1896, [ii.] 53, 225; *ibid.* 1897, [ii.] 56, 506; Ber. 1898, 31, 749; Poleck, *ibid.* 29; J. pr. Chem. 1897, [ii.] 56, 515; Erdmann and Huth, *ibid.* 1896, [ii.] 53, 42; Schimmel, Chem. Zentr. 1898, i. 258).

Rhodinol is probably identical with reuniol (Hesse, J. pr. Chem. 1896, [ii.] 53, 238; Erdmann and Huth, *l.c.*), but not with geraniol or *l*-citronellol.

Rhodinol combines with bromine to form a tetrabromide and with chlorine to form a dichloride (Monnet and Barbier, *l.c.*; Eckart, Arch. Pharm. 229, 355); from the latter, a *terpene*, b.p. 177°–178° has been obtained. When one drop of rhodinol is diluted with 5 c.c. of alcohol and 10 c.c. of concentrated sulphuric acid is then poured in, the acid sinks and becomes of an intense orange colour. On gentle shaking, the surface of contact of the two liquids assumes a reddish-violet colour. Linalool gives a similar reaction, but the colour rapidly turns brown; citronellol under the same conditions, gives a feeble colouration of a bluish tint (Erdmann, J. pr. Chem. 1897, [ii.] 56, 1). When oxidised, rhodinol yields: (1) an aldehyde, *rhodinal* $C_{10}H_{18}O$, mixed with menthone, b.p. of mixture 93°–95°/10 mm. Rhodinal does not combine with sodium bisulphite, but yields an oxime, b.p. 130°–135°/10 mm. and a semi-carbazone, m.p. 115° (Barbier and Bouveault, Compt. rend. 1896, 122, 529, 737; Bouveault, Bull. Soc. chim. 1900, [ii.] 23, 458, 463). (2) Dimethyl acetone; (3) β-methyl adipic acid. (4) *Rhodinolic acid* or *rhodinylic rhodinate* $C_{20}H_{36}O_2$, b.p. 190°/10 mm. (5) Valeric and possibly other acids (Barbier and Bouveault, Compt. rend. 1894, 119, 334; *ibid.* 1896, 122, 673; Barbier, *l.c.*: Eckart, *l.c.*).

The *rhodinol esters* formed by the action of acid chlorides on rhodinol in the presence of anhydrous pyridine, are liquids the odours of which decrease with increasing molecular weight (Erdmann, Ber. 1898, 31, 356; *see* also Charabot and Hebert, Bull. Soc. chim. [3] 13, 465).

Rhodinol opianate, m.p. 48·5° is obtained by heating rhodinol with opianic acid at 130°–135° (Erdmann).

Rhodinol semicarbazone has m.p. 112°, the *pyruvate*, b.p. 143°/10 mm. (Bouveault and Gourmand, *l.c.*).

For other rhodinol derivatives *see* Eckart, *l.c.*; Erdmann, *l.c.*; Erdmann and Huth, *l.c.*

Rhodinol is chiefly employed in perfumery (Pfister, Chem. Zeit. 1897, 38).

RHODIUM. Sym. Rh. At.wt. 102·9. Rhodium is contained in all native platinum and in the nickeliferous copper ores of Sudbury and elsewhere. It is distinguished from the other members of the platinum group by the rose-red colour of its salts, and would be of great importance if obtainable in quantity, on account of the fact that crucibles of rhodium have been found to be practically as resistant in all respects as iridium, whilst having little more than half the specific gravity of that metal (Crookes, Proc. Roy. Soc., 1908). Rhodium is obtained from the solution from which platinum has been precipitated as the double ammonium salt or as chloroplatinate. The mother liquors are decomposed with iron, and the resulting metallic precipitate is warmed with concentrated nitric acid, then with potash, after which the residue is mixed with sodium chloride and treated at a dull-red heat with a current of chlorine. The product is taken up with water, nitric acid is added to transform the iridium sesquichloride into iridium chloride, which is removed by precipitation with ammonium chloride. The solution contains the double chloride of rhodium and ammonium, which may be purified by repeated recrystallisation (Claus, J. pr. Chem. 1845, [i.] 34, 173).

Rhodium may also be isolated by melting the metallic precipitate containing it with 1 part of lead and 2 of litharge. The lead is then removed with nitric acid, and the residue is treated with sodium chloride and chlorine. The mass is taken up with water, and iridium is removed as above. The residue is evaporated to dryness to remove excess of ammonium chloride, after which the mass is warmed with 3–4 parts of sulphur. On cooling it is treated with *aqua regia* and concentrated sulphuric acid, which dissolves the rhodium. The rhodium so obtained is again subjected to the process as above described, and is finally converted into chloropentammine rhodium chloride, which may be obtained pure by conversion into its xantho salt or its nitrate, and reconverting into the chloropentammine. The latter when reduced with hydrogen, yields pure rhodium, which should be cooled in a current of carbon dioxide (Jorgensen, Zeitsch. anorg. Chem. 1903, 34, 82).

Numerous modifications of these processes have been described (Gibbs, J. pr. Chem. 1865, [i.] 94, 10; Lea, *ibid.* 95, 351; Schneider, Annalen, 1867, Suppl. 5, 261, amongst others).

Rhodium is a hard, white metal, ductile and malleable at a red heat. It has a sp.gr. of 12·1, fuses at about 1970° and, when pure, is insoluble in *aqua regia*, although it is attacked by chlorine and sulphur. It has the same power as platinum as a catalyst, but has not been commercially applied to that purpose. Its principal use is in the preparation of the thermo-couples for pyrometers, but its employment for the manufacture of crucibles is likely to increase (J. Ind. Eng. Chem. 1911, 3, 354). The thermo-electric properties of the rhodium-platinum element are discussed by Sosman (Amer. J. Sci. 1910, 30, 1); of rhodium-iridium by Broniewski and Hackspill (Compt. rend. 1911, 153, 814). Its salts have not received any technical application.

Colloidal rhodium may be obtained in the same way as colloidal iridium (Gutbier and Hofmeier, J. pr. Chem. 1905, [ii.] 71, 452). The colloidal metal colours a borax bead brown (Donan, Monatsh. 1904, 25, 913).

Rhodium Compounds.

Rhodium forms three oxides:—

Rhodium monoxide RhO is a grey powder, produced when the finely-divided metal is heated in air, or by heating the trihydroxide. It is not attacked by acids, but is reduced by hydrogen with evolution of light. A small quantity of it added to thoria-ceria mantles is said to considerably diminish the amount of ceria required (J. Soc. Chem. Ind. 1897, 37).

Rhodium sesquioxide Rh_2O_3 is formed as a grey iridescent mass by heating the nitrate, or as a crystalline mass when sodium rhodochloride is heated in oxygen. It is insoluble in acids. The corresponding *hydroxide* $Rh(OH)_3$ forms a heavy dark-brown mass when dry. It is almost insoluble in acids, and may be obtained by heating a solution of sodium rhodochloride with excess of caustic potash. If the potash is not in excess, the solution on standing deposits thin yellow crystals of the hydrate $Rh(OH)_3,H_2O$, which is soluble in acid, and, when freshly prepared, in alkalis. If chlorine be passed through the alkaline solution of the yellow salt, the colour changes from yellow to red, then a green precipitate is formed, which dissolves to a deep-blue solution, probably owing to the formation of the *per-rhodate* Na_2RhO_4 (Alvarez, Compt. rend. 1905, 140, 1341). The rhodium salts are derived from this oxide; they are of a dark red or yellow colour, and have a bitter taste.

Rhodium dioxide RhO_2, which closely resembles the sesquioxide, is obtained by repeated fusion with caustic potash and potassium nitrate. The corresponding tetrahydroxide $Rh(OH)_4$ is formed by the action of chlorine on the trihydroxide. It forms a green powder which yields a blue solution in hydrochloric acid, the colour gradually changing to red with evolution of chlorine.

Rhodium trichloride $RhCl_3$ may be obtained by igniting the metal in chlorine, or from the crude double chloride $RhCl_3{\cdot}3NaCl$ (formed by the action of chlorine on the metal in the presence of sodium chloride) by saturating its aqueous solution with hydrogen chloride, thus precipitating the sodium chloride, then evaporating the residue in a current of chlorine (Leidié, Compt. rend. 1899, 129, 1249). It may also be obtained by evaporating the tetroxide with hydrochloric acid (Gutbier and Trenkner, Zeitsch. anorg. Chem. 1905, 45, 166), and by other methods. Its colour and properties depend on its mode of preparation. It forms a large number of well-crystallised *rhodochlorides* or *chlororhodites* of the type M_3RhCl_6,xH_2O and also M_2RhCl_5,xH_2O (Gutbier and Trenkner, *l.c.*; Gutbier and Hüttinger, Ber. 1908, 41, 210).

The tribromide and iodide and their double salts have also been prepared (*see* above references and Goloubkine, Bull. Soc. chim. 1910, [ii.] 24, 388).

Rhodium monosulphide RhS, a bluish-white mass with a metallic lustre, is obtained by heating the metal in sulphur, or by passing sulphuretted hydrogen through a solution of a rhodium salt. If the latter process is carried out at 100°, the hydrosulphide $Rh(SH)_3$ is formed (Leidié, Compt. rend. 1888, 106, 1533).

The *sesquisulphide* Rh_2S_3 forms black crystalline plates produced by treating the trichloride with sulphuretted hydrogen at 360°. **Rhodium sulphate** $Rh_2(SO_4)_3$ and the sulphite $Rh_2(SO_3)_3$ have also been obtained.

Rhodium forms alums with the alkali metals, of the type $M_2SO_4,Rh_2(SO_4)_3,24H_2O$ (Piccini and Marino, Zeitsch. anorg. Chem. 1901, 27, 62).

Rhodium forms several series of ammoniacal derivatives, of which the three chief are:

Hexammine salts (Luteo salts)

$$[Rh(NH_3)_4]X_3.$$

Aquopentammine (Roseo salts)

$$[RhH_2O(NH_3)_5]X_3.$$

Pentammine (Purpureo salts)

$$[RhX(NH_3)_5]X_2,$$

where X is a negative radical. These salts resemble the corresponding cobalt salts.

Rhodium nitrate $Rh(NO_3)_3$, **nitrite** $Rh(NO_2)_3$, and its double salts, also **potassium rhodicyanide** $K_3[Rh(CN)_6]$, are known (Leidié, Compt. rend. 1890, 111, 106; 1900, 130, 87). Z. K.

RHODIZONIC ACID *v.* KETONES.

RHODOCHROSITE, or Manganese-spar. Native manganese carbonate $MnCO_3$ (47·7 p.c. manganese), crystallising in the rhombohedral system and isomorphous with calcite. Its characteristic colour is rose-red, hence the name rhodochrosite (not rhodochroisite), from ῥόδοχρως; another name in common use is dialogite—often misspelt 'diallogite.' Occasionally the colour is yellowish-grey or brown, due to the presence of iron; calcium, magnesium, zinc, or cobalt may also be present isomorphously replacing manganese. With these variations in composition the sp.gr. ranges from 3·0 to 3·6. In appearance, rhodochrosite somewhat resembles rhodonite (*q.v.*), from which it may be readily distinguished by its inferior hardness (H.=4) and by the fact that it effervesces in warm hydrochloric acid. The mineral usually occurs as granular or sparry masses showing a perfect rhombohedral cleavage, but occasionally crystals are found. These often have the form of rhombohedra with curved faces. Small clear crystals of scalenohedral habit are found in cavities in limonite near Horhausen in Rhenish Prussia; and magnificent rhombohedra associated with iron-pyrites come from Alicante, in Lake Co., and other localities in Colorado.

Rhodochrosite occurs in mineral-veins, together with ores of lead and silver; and as veins and beds in limestone. The most important deposit is that worked in limestone at Las Cabesses mine (dep. Ariège) in the Pyrenees, the output amounting to about 6000 tons per annum. It is also mined near Vielle Aure (dep. Hautes-Pyrénées), occurring here also in limestone and intimately intermixed with rhodonite and other manganese silicates. It is used for the manufacture of ferromanganese and spiegeleisen. When occurring with silver ores, as in Colorado, it is of value as a flux. L. J. S.

RHODODENDRIN. A glucoside $C_{16}H_{22}O_7$, found in the leaves of *Rhododendron chrysanthum* (Pall.). It is soluble in water, has a bitter taste, and melts at 187°.

RHODODENDROL $C_{10}H_{12}O_2$, a camphor-like decomposition product of rhododendrin, forms long colourless needles melting at 80° and subliming without decomposition (Archangelski, Chem. Zentr. 1901, [ii.] 594).

RHODONITE. Native manganese metasilicate, $MnSiO_3$, crystallising in the anorthic system and belonging to the pyroxene group of minerals. (Another native manganese silicate is the orthosilicate, Mn_2SiO_4, called tephroite and belonging to the olivine group; and several other mineral silicates contain manganese in combination with other metallic bases.)

Rhodonite, so named from ῥόδον, a rose, is typically of a rose-red colour, and usually forms granular to compact masses, with sp.gr. 3·5–3·6 and hardness 6. Such material is of value, when cut and polished, for ornamental purposes. The best quality is that quarried in black clay-slates at Ssedelnikova, near Ekaterinburg on the eastern slopes of the Urals. Boulders of similar material are found near Cummington in Massachusetts; and small blocks have been obtained in the Treburland manganese mine near Launceston in Cornwall. The invariable presence of veins and splashes of black manganese oxide (produced by the partial alteration of the material) form a pleasing contrast with the rich rose-red colour of the polished stone. Small brilliant crystals of rhodonite are found in the manganese mines at Filipstad in Sweden; and large rough crystals (of a zinciferous variety called fowlerite) are known from the zinc mines at Franklin Furnace in New Jersey. In the Pyrenees compact masses of rhodonite intimately intermixed with other manganese silicates and with rhodochrosite from beds in limestone: this material is mined (about 5000 tons per annum) at Vielle Aure (dep. Hautes-Pyrénées) for the manufacture of ferromanganese and spiegeleisen. Rhodonite is also used to a limited extent in pottery glazing and as a flux in smelting.

L. J. S.

RHŒADINE, RHEADINE, *v.* Vegeto-alkaloids.

RHUBARB, *Rheum officinale* (Baill.), and other species. A plant grown in the East for the sake of its rhizome, which is used in medicine (*v.* Rhubarb root), in temperate climates for the young stems which are used for table purposes. According to König, the following figures show the average composition of the edible stems—

	Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash
Large sticks	95·2	0·5	0·6	0·3	2·2	0·6	0·6
Small sticks	93·8	0·5	0·6	0·1	3·8	0·6	0·7

The large sticks contained 1·09 p.c. oxalic acid; the small, 0·5 p.c. According to Castoro (Landw. Versuchs. Stat. 1902, 56, 423), malic acid is also present in the stems. Calcium oxalate is found in the stems.

Quantities of rhubarb are grown in the neighbourhood of large towns, finding a large sale as a substitute for fruit, especially in the spring and early summer. Much of the rhubarb is 'forced' by being grown with the aid of heat, and is partially etiolated by whole or partial exclusion of light. In the open, crops up to 40 or 50 tons per acre of 'sticks,' can be grown by liberal nitrogenous manuring (*v.* Dyer and Shrivell, Jour. Royal Hort. Soc. 1903, 27, part 4). The quality of the product, especially its tenderness and succulence, is greatly enhanced by the use of sodium nitrate. When rhubarb is 'forced' by digging up the roots, keeping them in the cold until about Christmas and then placing them in darkened houses kept at about 60°–65°, much earlier and larger growth can be secured by first exposing the roots to ether vapour (10 c.c. ether per cubic foot of air) for 48 hours, before placing in the hothouse (Stuart, Rep. Vermont. Agric. Expt. Stat. 1903–1904, 442).

Rhubarb juice is used in the manufacture of a wine. According to Otto (Bied. Zentr. 1896, 128), a sample of the latter contains in grams per 100 c.c.:

Extract	Alcohol	Acid	Glycerol	Oxalic acid	Ash	Sp.gr. at 15°
2·412	3·94	0·748	0·547	0·067	0·397	1·0005

H. I.

RHUBARB RESIN *v.* Rhubarb-root.

RHUBARB-ROOT (*Rheum*; *Rhubarbe*, Fr.; *Rhabarber*, Ger.). The root of *Rheum palmatum* (Linn.), *Rheum officinale* (Baillon), and possibly other allied species, all inhabitants of Central Asia. For botanical characters *v.* Bentl. a. Trim. 213, 214; Flück. a. Hanb. 491; Pereira (Mat. Med. 1850, 2, 1343); also Flückiger (Neues Rep. Pharm. 25, 1), and Baillon (Pharm. J. [iii.] 3, 301). Attempts have been made from time to time to cultivate the official rhubarb plants in Europe which have been attended with a certain amount of success. Other allied species have also been grown. These have supplied the market with substitutes for the Chinese drug. The most important are *R. Rhaponticum* (Linn.), cultivated for a century in the neighbourhood of Banbury, and the same species, together with *R. palmatum* (Linn.), *R. undulatum* (Linn.), and *R. compactum* (Linn.), which are grown in France and Germany. The comparative value of English rhubarb has been studied by H. Senier (Pharm. J. [iii.] 8, 444) and Elborne (*ibid.* [iii.] 15, 136).

Rhubarb has been known from the very earliest times as a mild purgative and stomachic. Not only was its value appreciated by Dioscorides but in China its history goes back to the reign of the Emperor Shen-Nung, B.C. 2700. With the advent of chemical inquiry at the beginning of this century the composition of rhubarb was studied by numerous investigators. Of their results a summary is given by Pereira (Mat. Med., 1850, 2, 1355), but, with the exception of the identification of constituents which are common to most plants, this early work only resulted in the preparation of active but chemically indefinite extractives.

The first chemical investigation to give definite results of physiological importance was that of Schlössberger and Döpping (Annalen, 50, 213). These observers isolated *chrysophanic acid*, a yellow crystalline colouring agent which had already been found in the wall-lichen by Rochleder and Heldt (*ibid.* 48, 12), and which Liebermann (*ibid.* 183, 145) has shown to be a derivative of anthraquinone. Chrysophanic acid has also been obtained from *Squamaria elegans* (Thomson, *ibid.* 53, 260), *Rumex obtusifolius* (Linn.) (Thann, *ibid.* 107, 324), *Rumex Ecklonianus* (Meissner) (Tutin and Clewer, Chem. Soc. Trans. 97, 1), and from senna, *Cassia acutifolia* (Delile), and *C. angustifolia* (Vahl). De la Rue and Müller (Chem. Soc. Mem. 10, 298) discovered another crystalline colouring matter of a darker red-orange colour, *emodin.* This compound has also been found in the bark of *Rhamnus Purshiana* (De Cand.), *Cascara Sagrada*, and of *Rhamnus Frangula* (Linn.). According to Kubly (Pharm. Zeit. 6, 603; 24, 193: Pharm. J. [iii.] 16, 65) chrysophanic acid does not exist to any appreciable extent in rhubarb root, but is produced by the fermentation, in presence of water, of a glucoside *chrysophan.* This view is confirmed by Dragendorff (*ibid.* [iii.] 8, 826).

Many substances have been isolated from rhubarb by different workers. Most of these, however, are probably mixtures, and different names have been given to substances according to the state of purity in which they have been isolated. Among the more recent workers on this subject are Hesse (Annalen, 284, 191; 309, 32; J. pr. Chem. [ii.] 77, 32, 383); Tschirch and co-workers (Arch. Pharm. 240, 596; 243, 443; 245, 139; Chem. Zentr. 1904, i. 1077; 1905, ii. 144); Gilson (Compt. rend. 136, 385).

Among other substances, Chinese rhubarb contains *chrysophanic acid* associated with a compound stated by Hesse to be methylchrysophanic acid, but which is now known to be *emodin monomethylether* (Oesterle and Johann, Arch. Pharm. 248, 476); *emodin* which is identical with the emodin obtained from frangula; and *rhein* $C_{15}H_{10}O_6$, m.p. 312°–316°. *R. Rhaponticum* contains *rhapontin* (*rhaponticin*) $C_{21}H_{24}O_9$, m.p. 231°, with compounds similar to those found in Chinese rhubarb, but rhein and emodin are not present. From *R. palmatum*, there have been isolated emodin, *iso-emodin* (*rhabarberone*), and rhein, and from *R. officinale* (Baillon) the same compounds with the exception of emodin.

An examination of Shensi rhubarb has been made by Tutin and Clewer (Chem. Soc. Trans. 99, 946). An alcoholic extract of the drug, when distilled with steam, yielded small amounts of palmitic and chrysophanic acids together with a hexoic acid and some essential oil. The portion of the extract which was soluble in water yielded cinnamic and gallic acids, rhein, emodin, aloe-emodin, emodin monomethyl ether, chrysophanic acid and a new anthraquinone derivative *rheinolic acid* $C_{17}H_{10}O_6$, m.p. 295°–297°. It yielded also a crystalline mixture of glucosides of rhein, emodin, aloe-emodin, emodin-monomethyl-ether and chrysophanic acid, dextrose, lævulose, tannin, and an amorphous non-glucosidic resin. The resin on hydrolysis gave small quantities of gallic and cinnamic acids, rhein, emodin, aloe-emodin, emodin-monomethyl-ether and chrysophanic acid with a new compound $C_{14}H_{12}O_3$, m.p. 256°, probably a *trihydroxydihydroanthracene*. The portion of the extract insoluble in water yielded a trace of a *hydrocarbon*, m.p. 64°; a phytosterol (verosterol), $C_{27}H_{46}O$; a mixture of fatty acids; rhein, rheinolic acid, emodin aloe-emodin, emodin-methyl-ether, chrysophanic acid.

Chrysophanic acid is a dihydroxymethylanthraquinone, but the relative positions of the groups are not known with certainty. Emodin is a hydroxychrysophanic acid whilst emodin monomethylether is the corresponding methoxychrysophanic acid. Aloe-emodin (the rhabarberon of Hesse and the *iso*emodin of Tschirch and Eyken) is the primary alcohol (hydroxymethyldihydroxyanthraquinone), corresponding with chrysophanic acid, whilst rhein is the corresponding carboxylic acid, and may be formed by the oxidation of aloe emodin.

Of the anthraquinone derivatives only aloe-emodin and chrysophanic acid were found to have any purgative action, the mixture of glucosides being quite inert. The chief purgative principle is the non-glucosidic resin.

Müller (Chem. Soc. Trans. 99, 967) finds that rhubarb also contains alizarin.

A method for the valuation of rhubarb based on the amount of chrysophanic acid that can be obtained from it has been examined by Tschirch and Edner (Arch. Pharm. 245, 150). They found the following percentages of acid in the different varieties of rhubarb. Canton round, 3·9; Shanghai, 3·8; Canton flat, 3·0; Shensi flat, 3·0 and 2·7; Shanghai flat, 2·7; Canton II., 2·5; English, 2·0; French, 1·9; Austrian, 1·6.

For analyses of rhubarb see Dragendorff (Pharm. J. [iii.] 8, 826), H. G. Greenish (*ibid.* [iii.] 9, 933), Elborne (*ibid.* [iii.] 15, 137), Dessaignes (J. Pharm. Chim. [iii.] 25, 23), and for inorganic constituents Brandes (J. 1853, 581), Tip (J. 1854, 657), and Boni (Pharm. Post, 1888, 51). For rhubarb-testing see Maisch (Amer. J. Pharm. 43, 259), Howie (Trans. Brit. Pharm. Conf. 1873, 562), Husson (Union Pharm. 16, 99), H. G. Greenish (Pharm. J. [iii.] 9, 813), and Jaworowski (J. Pharm. Chim. [vi.] 8, 303).

A. S.

RICE, *Oryza sativa* (Linn.). A swamp grass which has been cultivated in Asia from remote ages. It is now extensively grown in Japan, China, India, the West Indies, Central America and the Southern United States. It forms the staple food of a very large proportion of the human race, but is chiefly used in the tropics.

Many varieties are known, some of which have been claimed as distinct species, *e.g.* *O. montana*, growing in dry soils at altitudes up to 6500 ft.; *O. glutinosa*, or viscous rice, and *O. præcox*, or quick-growing rice, which matures in about 3 months, as against 5 or 6 months required by other kinds. The grain with its adhering husk is known as 'paddy' but the rice imported into this country has had its outer brown husk removed.

According to König, the average weight of 100 grains of the three chief varieties is

	Viscous rice	Marsh rice	Hill rice
Unhusked	2·672	2·560	2·209 grms.
Husked	2·188	2·189	1·908 „

while the composition of the rice with husk is—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Viscous rice	12·6	5·1	3·0	73·4	4·5	1·3
Marsh rice	12·6	6·1	2·0	74·1	4·0	1·2
Hill rice	12·6	7·7	2·3	74·8	1·7	1·0

In various samples the protein varies from 5 to 10·5 p.c.; the starch from 72 to 80 p.c.

The rice deprived of its husk contains—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Japanese	11·1	8·5	1·9	76·0	1·0	1·5
East Indian	13·0	7·9	0·8	76·8	0·6	0·9
American	12·2	7·8	0·4	78·9	0·3	0·5

According to Wiley (Bull. 13 (1898) U.S. Dept. of Agriculture, 1182), the following figures represent typical samples:—

	Wt. of 100 grms. (grms.)	Water	Protein	Fat	Sol. carbohydrates	Crude fibre	Ash
Unhulled	3·00	10·5	7·5	1·6	67·4	9·0	4·0
Hulled	2·50	12·0	8·0	2·0	76·0	1·0	1·0
Hulled and polished	2·20	12·4	7·5	0·4	78·8	0·4	0·5

A large number of samples from Burmah, Carolina, India, Japan, Java, Piedmont, and Cochin China, examined by Balland (Compt. rend. 1895, 121, 561), yielded the following figures:—

	Water	Protein	Fat	Starch, etc.	Crude fibre	Ash
Crude, Max.	13·3	9·1	2·5	75·6	2·4	2·2
„ Min.	11·2	6·2	1·9	73·8	0·9	1·2
Decorticated, Max.	16·0	8·8	0·7	81·4	0·4	0·6
„ Min.	10·2	5·5	0·2	75·6	0·2	0·4

Balland found the acidity to lie between 0·03 and 0·06 in the refined rice, between 0·04 and 0·09 in the crude rice, while the sugars were 0·15–0·50 in the former and from 0·56 to 0·90 in the latter. Decortication greatly reduces the fat, nitrogenous matter, and ash, while polishing still further diminishes these constituents.

The proteids of rice (7 p.c.) contain a glutenin, *oryzenin*, soluble only in dilute alkali, about 0·14 p.c. of a globulin and 0·04 p.c. of an albumin (Rosenheim and Kajiura, Proc. physiol. Soc. 1908, 54). According to Suzuki, Yoshimura, and Fuji (J. Coll. Agric. Tokyo, 1909, 1, 77) the dry matter of rice, freed from husks, contained total nitrogen 1·200 p.c., of which 1·165 p.c. existed as true proteids. The cleavage products of the proteids were examined and estimated. They consisted largely of glutamic acid, 14·5 p.c.; leucine, 14·3 p.c.; alanine, 3·7 p.c.; proline, 3·3 p.c.; arginine, 1·6 p.c.; phenylalanine, 2·0 p.c.; ammonia, 2·33 p.c., with smaller quantities of lysine, histidine, and tyrosine.

Rosenheim and Kajiura attribute the unsuitabliity of rice for making dough and bread to the almost complete absence of an alcohol-soluble protein (gliadin). The prolonged use of an exclusive rice diet tends to the outbreak of the disease, beri-beri; but this tendency can be destroyed by the addition to the diet of barley meal. They suggest that the increased supply of glutamic acid in hordein (from 35 to 41 p.c.) may partly explain this.

The oil of rice was examined by Brown (J. Amer. Chem. Soc. 1903, 25, 948), who found indications of the presence of a fat-splitting enzyme in rice bran, to which he attributes the high proportion of free fatty acids, often found in oil from old rice. The germ and gluten layer of rice were found to contain about 15 p.c. of oil of sp.gr. $\frac{99^\circ}{99^\circ}$ 0·8907, m.p. 24°, acid value, 166·2; saponification value, 93·5; iodine value, 91·6; Reichert-Meissl value, 1·1; mol. equiv. of insoluble fatty acids 289·3, and m.p. of insoluble fatty acids 36°.

The ash of rice is rich in phosphoric acid and potash; analyses of the ash of Japanese rice by Kellner (*l.c.*) gave the following figures:—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Marsh rice	22·9	4·9	3·2	10·5	1·0	51·4	1·9	3·1	1·0
Hill rice .	21·7	1·6	2·1	6·6	1·7	52·0	2·1	9·6	4·5

Rough rice, as produced by the planter, when sent to the mills, yields about 18 p.c. chaff and waste, 18 p.c. rice bran, 5 p.c. 'rice polish,' and 59 p.c. of clean rice.

Rice straw has some value as a fodder. Analyses of straw (1) from a good harvest and (2) from a poor harvest were made by Takeuchi (Bull. Coll. Agr. Tokyo 1908, 7, 619)—

	Dry matter	N	Fat	Dextrose	Sucrose	Starch	Pentosans	Fibre	Ash
1 .	87·69	0·97	1·36	2·25	0·79	14·86	14·28	31·16	5·39
2 .	90·15	1·48	1·65	3·28	0·96	18·75	16·55	28·72	6·13

Rice bran and rice polish are valued as cattle foods. 'Rice meal' or 'rice feeding meal' consists of ground rice bran or a mixture of the bran and 'polish,' or sometimes largely of much less valuable ground chaff. Both bran and polish are rich in oil and albuminoids.

The following are analyses of various milling products of rice:—

	Water	Protein	Fat	N-free extract	Crude fibre	Ash
Husks . .	10·0	3·7	1·4	32·3	38·1	14·5
Bran (Rangoon)	9·1	13·3	15·5	47·0	6·2	10·1
Polish . .	9·5	11·6	10·1	63·9	0·6	4·5

For results of recent analyses of 159 samples of various Indian rice, *v.* Hooper (Agric. Ledger, 1908–1909, 5, 63).

Rice is used in the production of an alcoholic beverage, *sakè*, in Japan, and in the preparation of starch. The starch granules of rice resemble those of the oat, but are smaller (the average diameter of the simple grains being about 5μ, whilst those of the oat are about 10μ) and more angular. Compound grains made up of aggregations of the simple grains occur in the seed, but are very readily broken up on treatment with water, and occur very rarely in commercial rice starch.
H. I.

RICINELAIDIC ACID, RICINOLEIC ACID *v.* OILS, FIXED, AND FATS.

RICINUS OIL *v.* CASTOR OIL; also OILS, FIXED, AND FATS.

RINMANN'S GREEN *v.* COBALT.

RIONITE. A bismuth fahlore found at Cremenz, in the Canton Wallis.

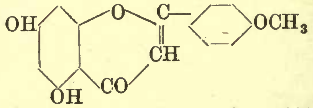
ROBINIA PSEUD-ACACIA (Linn.) *Acacetin* $C_{16}H_{12}O_5$, the colouring matter of the leaves of the *R. Pseud-acacia* (common or false acacia, North American locust), forms almost colourless needles, soluble in alkalis with a pale yellow colouration (Perkin, Chem. Soc. Trans. 1900, 71, 430).

A boiling aqueous decoction of the leaves is treated with basic lead acetate solution, and the pale yellow precipitate is suspended in water and decomposed with boiling dilute sulphuric acid. From the clear liquid the colouring matter is removed by extraction with ether and purified by crystallisation from dilute alcohol.

Acacetin forms a *diacetyl* derivative

$$C_{16}H_{10}O_5(C_2H_3O)_2$$

colourless needles, m.p. 195°–198°, and when fused with alkali gives *phloroglucinol* and *p-hydroxybenzoic acid.* Digested with boiling hydriodic acid it yields apigenin and one molecule of methyl iodide, and is consequently an *apigenin monomethylether.* Acacetin is very probably identical with von Gerichten's apigenin methyl ether (Ber. 1900, 33, 2908)



the acetyl derivative of which melts at 198°–200°.
A. G. P.

ROBININ *v.* GLUCOSIDES.

ROBURITE *v.* EXPLOSIVES.

ROCCELLA *v.* ARCHIL AND LICHENS.

ROCCELLIN *v.* AZO- COLOURING MATTERS.

ROCELLIC ACID $C_{15}H_{30}(CO_2H)_2$. Obtained from various lichens, from *Rocella fuciformis* and *R. tinctoria* (Hesse, J. pr. Chem. [ii.] 57, 261), *Lecanora sordida* (Hesse, *ibid.* 58, 497), *L. cenisea* and *Lepraria latebarum* (Zopf, Annalen, 295, 264, and 298); white silky plates, m.p. 127°–128°. The anhydride is an oil (*cf.* Schunck, Chem. Soc. Trans. 1848, 3, 153), *v.* LICHENS.

ROCHELLE SALT *v.* TARTARIC ACID.

ROCK, ALUM. *Alunite v.* Alums.

ROCK-CRYSTAL *v.* Quartz.

ROCK OIL *v.* Petroleum.

ROCK SALT *v.* Sodium chloride.

ROCK-PHOSPHATE *v.* Phosphorite.

RODAGEN *v.* Synthetic drugs.

RODINAL. A solution of *p*-aminophenol, used as a photographic developer.

ROMAN ALUM *v.* Alums.

ROMAN CEMENT *v.* Cement.

ROMAN LAKE. *Crimson lake v.* Pigments.

ROMAN OCHRE. A variety of argillaceous ferric oxide of an orange-yellow colour, used as a pigment.

ROMITE *v.* Explosives.

RONGALITE. Trade name for sodium formaldehyde sulphoxylate.

ROSANILINE and **ROSANILINE DYES** *v.* Triphenylmethane colouring matters.

ROSCOELITE or Vanadium-mica. A member of the mica group of minerals (*q.v.*) similar to muscovite in composition but with alumina largely replaced by vanadous oxide (V_2O_3 reaching 28·85 p.c.). It occurs in some abundance as sage-green scaly masses, intimately associated with native gold and gold tellurides, in Eldorado Co. in California, in the Magnolia and Cripple Creek districts in Colorado, and at Kalgoorlie in Western Australia. In larger quantities it occurs, together with carnotite (*q.v.*), as an impregnation in Jurassic sandstone near Placerville in San Miguel Co., Colorado. The roscoelite forms up to 20 p.c. of the mass of the sandstone in a bed varying from a few inches to 5 or 6 ft. in thickness. Analyses by W. F. Hillebrand (Amer. J. Sci. 1899, 7, 451; 1900, 10, 120): I. from Granite Creek, Eldorado Co., California; II. from Placerville, Colorado.

	I.	II.
SiO_2 . . .	45·17	46·06
TiO_2 . . .	0·78	—
V_2O_3 . . .	24·01	12·84
Al_2O_3 . . .	11·54	22·55
Fe_2O_3 . . .	—	0·73
FeO . . .	1·60	—
CaO . . .	—	0·44
BaO . . .	—	1·35
MgO . . .	1·64	0·92
K_2O . . .	10·37	8·84
Na_2O . . .	0·06	0·22
H_2O (105°) . .	0·40	1·98
H_2O (>105°) . .	4·29	4·07
	99·86	100·00

Attempts have been made at Newmire, Colorado, to utilise this roscoelite-bearing sandstone as a source of vanadium.

L. J. S.

ROSE ATTAR *v.* Oils, essential.

ROSE OIL *v.* Oils, essential.

ROSE PINK. A pigment prepared by dyeing whiting with Brazil wood. It is too fugitive for artistic use, but is much employed in paper-staining.

ROSEÏNE. A synonym for fuchsine or aniline-red: *v.* Triphenylmethane colouring matters.

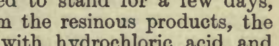
ROSEMARY OIL *v.* Oils, essential.

ROSENTHIEL'S GREEN or **CASSEL GREEN.** *Barium manganate.* It is also known as *manganese green.* It is a very unstable pigment.

ROSEWOOD, OIL OF. A volatile oil obtained from the wood of *Convolvulus scoparius* by distilling with water. A light-yellow oil consisting mainly of a terpene $C_{10}H_{16}$: b.p. 249°. Used occasionally for adulterating oil of roses, *v.* Oils, essential.

ROSHYDRAZINE. The colour and leuco-bases of triphenylmethane, when diazotised and treated with $SnCl_2$, are readily converted into hydrazines. For example: Rosaniline (5 grms.) is dissolved in 30 c.c. of hydrochloric acid and 70 c.c. of water, and the iced solution is diazotised by adding 3½ grms. $NaNO_2$ in 10 c.c. of water. On mixing the solution of the diazo compound with a well-cooled solution of 12 grms. of tin in 30 c.c. of hydrochloric acid, the *roshydrazine hydrochloride* separates in green, shimmering crystals. The salt is easily soluble in water, nearly insoluble in hydrochloric acid. Its solution has a bluer shade than rosaniline; it is a strong colouring matter, and dyes tannined cotton a deep brownish-red. Like other hydrazines, it reduces Fehling's solution, and forms condensation products with aldehydes and ketones. The latter compounds are sparingly soluble dyestuffs; thus acetone, aldehyde, pyruvic acid, benzophenone, &c., give reddish to bluish-violet colours; acetoacetic ester and benzaldehyde give blues; whilst glucose gives a greyish-blue. Benzaldehyde sulphonic acid yields a blue soluble in water. These condensation products can also be formed upon the fibre. The reduction of the diazo compound of acid-magenta gives rise to easily-soluble sulphonic acids of roshydrazine, the condensation products of which are soluble colouring matters. Safranine, when treated in the same way, does not give a hydrazine, but evolves nitrogen (J. H. Ziegler, Ber. 1887, 20, 1557; J. Soc. Chem. Ind. 6, 594).

ROSIN OIL, ROSIN SPIRIT *v.* Resin oil.

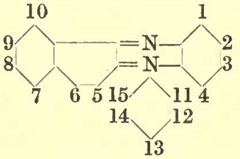


ROSINDULINE $NH{:}C_{10}H_5{<}\genfrac{}{}{0pt}{}{N}{NPh}{>}C_6H_4$ is prepared by heating benzeneazo-α-naphthylamine hydrochloride (1 part) with aniline (2 parts) and alcohol (4 parts) under pressure at 160°–170° for 6–8 hours. The alcohol is then evaporated and the excess of aniline is distilled off with steam. The residue is filtered and then extracted several times with boiling water. The combined filtrates are allowed to stand for a few days, then decanted from the resinous products, the solution acidified with hydrochloric acid and precipitated with sodium chloride, when the hydrochloride separates in long red needles, from which the base may be obtained by decomposing with soda and extracting with ether (Fischer and Hepp, Annalen, 1890, 256, 233; D. R. P. 71296). It may also be obtained by passing a stream of air through, and warming an alcoholic solution of phenylnaphthaphenazonium sulphonic acid to which ammonia has been added (Kehrmann and Locher, Ber. 1898, 31, 2430; Kehrmann and Schaposchnikoff, *ibid.* 1897, 30, 2627). For other methods of preparation, see Kehrmann and Messinger, *ibid.* 1891, 24, 587, 2167; Fischer and Hepp, *ibid.* 1896, 29, 2760; Annalen, 1895, 286, 227; Kehrmann, *ibid.* 1896, 290, 268).

Rosinduline forms reddish-brown plates,

m.p. 198°–199°, readily soluble in ether, benzene or alcohol; insoluble in water: readily absorbs carbon dioxide from the air and is decomposed by concentrated hydrochloric acid forming ammonia and rosindone. It forms salts with the mineral acids, and yields the *hydrate* $C_{22}H_{15}N_3,H_2O$, m.p. 185°–187°. When the base is diazotised in strong acid solution, and then treated with alcohol, it forms naphthaphenazonium. Unlike *iso*rosinduline, it does not combine with tetramethyldiaminobenzhydrol. According to Kehrmann (Ber. 1894, 27, 3348; *ibid.* 1896, 29, 2316, 2967; Annalen, 1896, 290, 247), rosindulines are *o*-quinoidal azonium compounds, but Fischer and Hepp regard them as derivatives of α β-naphthaphenazine (Annalen, 1892, 272, 306; Ber. 1896, 29, 361, 2752).

The effect of introducing the amino group into rosinduline in different positions has been studied by Kehrmann, Rademacher and Feder (Ber. 1898, 31, 3076), who have found, that representing the scheme of numbering thus,



the introduction of an amino group into the para position (2) with respect to the azonium nitrogen gives a bluish-violet dyestuff with scarcely any fluorescence. On the other hand, an amino group at 13 or in any position of this phenyl group causes hardly any increase in the depth of shade, the diamine 6 : 13, scarcely differing in colour from rosinduline which has an amino group at 6, whilst the triamines, 2 : 6 : 13, 2 : 6 : 12, are bluish-violet and differ little from the diamine 2 : 6. The introduction of an amino group para to the azine nitrogen at 3 causes little alteration in shade, but increases the tinctorial value of the colour and the fluorescence. These facts are analogous to those known for the safranines of the benzene series.

A number of nitro- and amino-rosinduline chlorides have been prepared (*see* also Kehrmann, Chem. Zentr. 1900, ii. 813).

Ethylrosinduline may be obtained in the same way as rosinduline by using benzeneazo-α-ethyl naphthylamine. It has m.p. 184°, gives a green solution in sulphuric acid, which turns red on addition of water and like rosinduline it is a good dye.

Methylrosinduline is obtained by boiling the anhydride of phenynaphthaphenazonium sulphonic acid with methylamine in alcohol (Kehrmann and Locher, *l.c.*). It forms gold coloured leaflets, m.p. 180°–181°, and behaves like the ethyl derivative with sulphuric acid.

Phenylrosinduline may be prepared by heating 5·8 grms. *p*-nitrobenzeneazo-α-naphthylamine with 15 grms. of aniline at 160°–165° for 2 hours (Paul, Chem. Zentr. 1897, i. 1168); by heating α-nitronaphthalene with aniline and aniline salts (D. R. PP. 67339, 45370) and by many other methods (Kehrmann and Locher, *l.c.*; Fischer and Hepp, Ber. 1888, 21, 2621; 1897, 30, 1829; Annalen, 1890, 256, 233). It forms dark-red needles, m.p. 234°, almost insoluble in water and sparingly soluble in organic solvents. Its neutral salts are red, whilst the acid salts are green, the dyeing properties of the hydrochloride being analogous to the fuchsine dyes. With concentrated sulphuric acid it forms an almost insoluble *monosulphonic acid*, whilst with fuming sulphuric acid it gives a *di-sulphonic acid* known as *azocarmine*; a trisulphonic acid readily soluble in water known as *rosinduline 2B* has also been obtained (D. R. PP. 52922, 79953, 59180, 64993, 67198, 72343; Eng. Pat. 8184, 1894).

Hydroxyphenylrosindulines, from which sulphide dyes have been prepared, are obtained by heating *p*-amino-*o*-cresol with benzeneazo-α-naphthylamine in water or alcohol (D. R. P. 158077; J. Soc. Chem. Ind. 1906, 175).

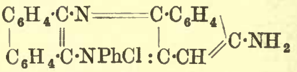
Trihydroxyphenylrosinduline may be prepared from substances such as the dyestuffs obtained by combining diazo- compounds with α-naphthylamine by heating with *p*-amino phenol and hydrochloric acid or by treating 1 : 4 naphthalene diamine similarly and oxidising the product with an aromatic nitro compound: also by heating α-nitronaphthalene with *p*-aminophenol and hydrochloric acid (D. R. PP. 158077, 158100, 160789).

When benzeneazomonoaryl -α- naphthylamines or monoaryl-1 : 4-diaminonaphthalene replaces the benzeneazo-α-naphthylamine, the resulting dyestuffs are said to produce purer and bluer shades (D. R. P. 160815).

Halogen and other derivatives of phenylrosinduline have been prepared, many of which are also used in dyeing.

o-*Tolylrosinduline* can be obtained by heating rosindone with *o*-toluidine and its hydrochloride at 150°–170° (D. R. PP. 15894, 67115). It forms readily soluble sulphonic acids with fuming sulphuric acid: p-*tolylrosinduline* (D. R. P. 65894; Fischer and Hepp, *l.c.*), *naphthylrosinduline* (D. R. P. 71296; Fischer and Hepp, *l.c.*), have also been prepared.

Phenanthrarosinduline

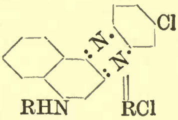


$$\begin{array}{l} C_6H_4\cdot C\cdot N{=\!=\!=}C\cdot C_6H_4\diagdown \\ \quad C\cdot NH_2 \\ C_6H_4\cdot C\cdot NPhCl : C\cdot CH\diagup\!\!\diagup \end{array}$$

is prepared by the action of ammonia and air on naphthaflavinduline chloride. It crystallises in dark red prisms with a bronze-like lustre (Kehrmann and Eichler, Ber. 1901, 34, 1210).

Phenylphenanthrarosinduline is prepared by the action of aniline on naphthaflavinduline and forms large dark violet crystals with a copper-like lustre (Kehrmann and Eichler, *l.c.*).

Chloro- substituted rosindulines of general formula



have been formed by condensing chloro- derivatives of substituted *o*-diamines of the general formula

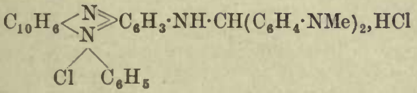
$$C_6H_3Cl(NH_2)NHR(1:4:2)$$

(R=aromatic or aliphatic radicle) with 4-amino and 4-anilino β-naphthaquinone. These dyestuffs give blue shades and when treated with amines are converted into safranine dyestuffs (Eng. Pat. 14238, 1899; J. Soc. Chem. Ind. 1900, 530).

iso-*Rosindulines.* This name was originally applied to the rosindulines having the NH group in the phenyl portion of the molecule and the 3-NH derivative, $C_{10}H_6N{\cdot}NPh{\cdot}C_6H_3NH$ (see above), was first prepared by Nietzki and Otto (Ber. 1888, 21, 1601) by warming an alcoholic solution of phenyl-β-naphthylamine (1 mol.) with quinonedichlorimide. It is a bluish-violet powder forming violet solutions in alcohol and ether.

*Phenyl*iso*rosinduline* is obtained by the action of nitrosodiphenylamine and phenyl-β-naphthylamine (Fischer and Hepp, Ber. 1896, 29, 2753) or by allowing an alcoholic solution of chlorophenylnaphthazonium chloride and aniline to stand for several hours (*ibid.* 1898, 31, 304; *ibid.* 1900, 33, 1496). It forms copper coloured crystals, m.p. 169°–171°, gives a blue solution in benzene and alcohol and is converted into *iso*rosindone when heated with glacial acetic and hydrochloric acids at 235°.

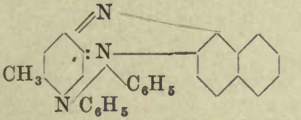
*Iso*rosinduline chloride reacts with tetramethyldiaminodiphenylbenzhydrol, forming a leucauramine,



$$C_{10}H_6\underset{\displaystyle Cl\quad C_6H_5}{<{}^{N}_{N}\geqslant} C_6H_3{\cdot}NH{\cdot}CH(C_6H_4{\cdot}NMe)_2,HCl$$

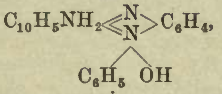
from which dyestuffs can be obtained giving red yellow shades on cotton mordanted with tannin (Mohlau and Schaposchnikoff, Ber. 1900, 33, 799).

*β-o-Methylphenyl*iso*rosinduline*



may be obtained by boiling an alcoholic solution of β-*o*-methylchlorophenylnaphthaphenazonium chloride with 2 molecular proportions of aniline for several hours. It forms coppery crystals which give a blue solution in sulphuric acid. The corresponding tolyl rosinduline, m.p. 226°, and the β-naphthyl compound, which is a reddish-violet dyestuff, are prepared similarly (Fischer, Ber. 1901, 34, 940).

Kehrmann has, however, applied the term *iso*rosinduline to the base,



$$C_{10}H_5NH_2\underset{\displaystyle C_6H_5\quad OH}{\leqslant{}^{N}_{N}>}C_6H_4,$$

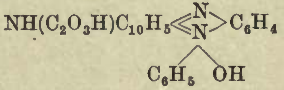
the NH_2 group occupying any one of the 15 positions in the naphthyl, or either of the phenyl groups, and he has prepared 15 such chloro-derivatives of *iso*rosinduline (aminophenylisonaphthaphenazonium chlorides), of which two or three may be mentioned as examples. Their number refers to the order in which they were prepared, not to the position of the NH_2 group.

iso-*Rosinduline, No.* 5 (2-aminophenyl naphthaphenazonium chloride), exists in two modifications. The labile form is obtained by reducing 2-nitrophenylnaphthaphenazonium chloride with tin chloride and hydrochloric acid at 0°. It gives reddish-violet solutions in alcohol and in water. On addition of dimethylamine to the former solution it turns green, then passes into blue and finally becomes fuchsine red. The stable form is prepared by carrying out the above reduction without any artificial cooling. It forms a dirty violet aqueous solution and a blue alcoholic solution which becomes fuchsine red on addition of dimethylamine (Kehrmann and Valencien, Ber. 1900, 33, 409).

iso-*Rosinduline, No.* 12, the 8 amino-derivative is obtained thus: phenyl*iso*naphthaphenazonium nitrate is treated with conc. nitric acid, and the two-mononitro derivatives thus obtained are extracted with alcohol, precipitated with ether and reduced with tin chloride and hydrochloric acid. The tin double compound is oxidised in alcoholic solution with ferric chloride, the precipitate dissolved in water, treated with sodium acetate and then with sodium bromide. The bromide of No. 10 *iso*rosinduline is removed by solution in a little hot water and a saturated solution of sodium bromide is then added, when the bromide of No. 12 separates as steely almost black prisms sparingly soluble in cold, readily so in hot water and giving a brown-red solution in sulphuric acid which turns orange-yellow on dilution and dirty greenish-blue on neutralisation (Kehrmann and Steiner, Ber. 1900, 33, 3276).

iso-*Rosinduline. No.* 15 (12-aminophenylnaphthazonium chloride) is formed by the interaction of 4 : 1 : 2-aminonaphthaquinone and 2 : 3′diaminodiphenylamine in the presence of a drop of dilute hydrochloric acid. The product is converted into the diacetyl derivative which, on boiling with hydrochloric acid in alcoholic solution, yields 6 : 12-diaminophenylnaphthaphenazonium chloride. The latter is converted into the acetyl derivative, diazotised, treated with sodium bromide and then hydrolysed with sulphuric acid when the desired compound separates in dark, yellow-brown greenish metallic granules, sparingly soluble in water and giving a violet solution in sulphuric acid. The solutions are non-fluorescent and have a bitter taste (Kehrmann and Nüesch, Ber. 1901, 34, 3099). The dichromate forms lustrous golden-yellow laminæ.

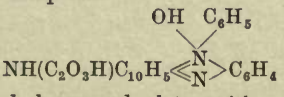
*Acetyl*iso*rosinduline* exists in two modifications: the α-compound,



$$NH(C_2O_3H)C_{10}H_5\underset{\displaystyle C_6H_5\quad OH}{\leqslant{}^{N}_{N}>}C_6H_4$$

forms red needles, with a green metallic lustre which decompose at 290°. It forms a yellowish-red fluorescent solution in alcohol and when boiled with hydrochloric acid it yields rosinduline salts.

The β-compound



$$NH(C_2O_3H)C_{10}H_5\overset{\displaystyle OH\quad C_6H_5}{\leqslant{}^{N}_{N}>}C_6H_4$$

forms dark brown-red plates with a metallic lustre which decompose at 260°, more readily soluble in alcohol than the α-compound, the solutions being dark red and non-fluorescent. When boiled with hydrochloric acid it yields an *iso*rosinduline salt (Kehrmann and Hertz, Annalen, 1896, 290, 262; Kehrmann and Aebi, Ber. 1899, 32, 932).

For the other *iso*rosindulines, see Kehrmann and Ravinson (Ber. 1899, 32, 927); K. and

Filatoff, *ibid.* 2627); K. and Levy (*ibid.* 1898, 31, 309); K. and Denk (*ibid.* 1900, 33, 3295); K. and Wolff (*ibid.* 1543); K. and Silberstein, 3300); K. and Misslin (*ibid.* 1901, 34, 1224); K. and Ott (*ibid.* 3092).

For other literature on rosinduline and *iso*-rosinduline and their derivatives, *v.* Fischer and Hepp (Annalen, 1890, 262, 237; Ber. 1900, 33, 1485); Kehrmann and Schaposchnikoff (*ibid.* 1896, 29, 2967; *ibid.* 1897, 30, 1565); Schraube and Romig (*ibid.* 1893, 26, 575); Kehrmann and Hiby (*ibid.* 1901, 31, 1085); Kehrmann and Silberstein (*ibid.* 1900, 33, 3280, 3285). Also the references already given.

ROSINS *v.* RESINS.

ROSOCYANIN *v.* TURMERIC.

ROSOLIC ACID *v.* AURINE.

ROSOPHENINE 10 B. *v.* PRIMULINE AND ITS DERIVATIVES.

ROTTENSTONE. A disintegrated rock which, when washed and ground, is used as a polishing material for metal, marble, &c. It is usually regarded as the residual matter left on the natural decompositions of impure limestone. If the limestone be silicious, the silica may be left in a very finely-divided condition; but old analyses of Derbyshire rottenstone show a very large proportion of alumina. The rottenstone of Derbyshire occurs in irregular cavities in the carboniferous limestone, and the best kinds are said to be obtained from a black bituminous limestone near Ashford, and on Bakewell Moor. It has also been worked in South Wales, especially in the counties of Brecon, Carmarthen, and Glamorgan. The term 'rottenstone' is sometimes applied to *tripolite*, a material consisting of highly-comminated silica, which is mostly derived from the frustules or silicious cases of the unicellular algæ known as diatoms. It is therefore similar to diatomaceous earth or kieselguhr (*q.v.*).

ROTTLERIN *v.* RESINS.

ROUGE *v.* *Iron oxides*, art. IRON.

ROUILLE *v.* *Iron oxides*, art. IRON.

ROYAL BLUE. *Smalt v.* COBALT; also PIGMENTS.

RUBBER (*India-rubber, Caoutchouc*) is a substance possessing peculiar and valuable physical, mechanical (tensile), and chemical properties, by virtue of which it is widely employed in numerous industries and arts and for many domestic purposes. The main constituent of the commercial article is a hydrocarbon possessing the empirical formula $(C_5H_8)n$ or $(C_{10}H_{16})n$. Rubber is generally derived by a process of coagulation from a fluid (*latex*) contained in a special cell system (*laticiferous system*) of various trees, creepers, and shrubs. It also occurs occasionally in the solid state, in the form of a deposit in the woody fibre of certain species, for instance in *Parthenium argentatum* (guayule). The laticiferous system, which is distinct from the sap-bearing cell system, generally liesbetween the outer bark and the cambium, and by cutting through the former and into the latex cells, the latex is obtained in the form of a white to cream coloured, more or less viscous fluid. This operation is termed 'tapping.' The rubber is contained in the latex in the shape of small particles (varying according to species from roughly 0·5 to 4μ in diameter), which are generally suspended in the serum in the form of a negative emulsion. The rubber is separated from the latex either by evaporating a part of the water or by a process of coagulation which varies according to the species, district, &c. After the coagulum has been separated from the serum it is generally purified and dried to a greater or less extent, and is then exported in the form of balls, loaves (*fine Para*), sheets, crepe, block (plantation species), slabs, irregular lumps, 'sausages,' 'thimbles,' &c.

Rubber-bearing species. The chief orders, genera, and species are shown on page 583.

Collection of latex and *coagulation.* In the Amazon district from which the 'fine Para' brands of commerce are obtained, the methods employed are briefly as follows: The trees are tapped with a small axe (machadinha), the incisions taking the form, generally, of V cuts or oblique lines. The first tappings are made at a height of 6–7 ft., subsequent incisions at intervals of roughly 1½–2 ins. beneath the first one, until the base of the tree is reached. This process is then repeated, the next tapping line (arraçao) commencing at a horizontal distance of about 18 ins. from the first one. The latex is collected in small tin or earthenware cups fixed to the tree by means of moist clay. The daily yield of latex from a mature tree is stated to be about 1½ oz., which corresponds roughly to 5 lbs. of rubber per tree per season, but it is doubtful whether any large proportion of the forest trees show as high a yield as this over a succession of seasons. After the *seringueiro* (as the rubber worker is termed) has completed his tapping round, he covers the same ground again in order to collect the latex. From the cups the latter is transferred to pails, thence to flat basins, and is subsequently cured by a smoking process which is carried out in the following manner:—

In a small brazier a fire is made, consisting largely of material giving a dense smoke rich in the products of dry distillation of woody matter (creosote, tarry matter, acetic acid). For this purpose the fruit (nuts) of the *urucuri* palm (*Attalea excelsa* [Mart.]) are considered particularly suitable. A mandril, consisting of a long wooden rod or paddle is so disposed, one end on a cross piece, the other on the operator's knees, that it can be rolled either over the top of the chimney—and so be exposed to the full volume of smoke—or over the basin containing the latex. The operator then pours a small quantity of latex over the wooden paddle or rod, thus forming a thin film of liquid. This is rotated in the smoke until it sets. A fresh quantity of latex is then poured on to the first film, smoke is again applied, and so on, until a biscuit or ball of rubber of the required size (20–100 lbs. is the general average weight) consisting of innumerable thin layers tightly adhering to one another, is formed. The ball is then removed from the mandril and is ready for export, forming the 'fine Para' of commerce.

'Up-river' (*i.e.* above Manaos) 'fine Para' is generally of the type termed *hard cure*, 'Islands' rubber (*i.e.* that from the mouth of the Amazon) generally as *soft cure.* The main difference is that indicated by the names. Imperfectly cured loaves are known as *entre-fine.* The scrappy rubber formed by premature coagulation on the tree or in the collecting or

Order	Genus	Species	Occurrence, etc.
Euphorbiaceæ .	Hevea	brasiliensis (Muell. Arg.)	*South America,* particularly *Brazil;* employed practically to exclusion of all other trees on Eastern plantations. Forms *Para* rubber of commerce.
,, .	Manihot	Glaziovii (Muell. Arg.); dichotoma	*Ceará* (*Brazil*); planted to some extent in Africa and tropical America. Forms the *Ceara* or *Manicoba* rubber of commerce.
,, .	Sapium	Tolimense; verum, &c.	*Central and South America* (*Colombia Virgen; Carthagena Scraps,* &c. of commerce).
Apocynaceæ .	Funtumia	elastica (Stapf)	*Tropical Africa;* forms *Gold Coast Lumps, Ivory Coast Lumps,* and various '*niggers,*' &c. of commerce. Planted in some parts of Africa.
,, .	Landolphia	owariensis (Beauv.); Heudelotii D.C. Thollonii (Dew.); sphaerocarpa (Jumelle); Pierrei	Creepers occurring in enormous quantities in *Tropical Africa,* forming many of the 'Congo' varieties, '*Madagascars,*' &c. of commerce.
,, .	Clitandra	Numbers of species of this genus are distributed in many parts of *tropical Africa,* principally Gold Coast and Congo	
,, .	Hancornia	speciosa (Gomez) (Muell. Arg.)	*Brazil* (Bolivia and Pernambuco) yields the '*Mangabeira,*' *Bahia,* and *Matto-grosso sheets* of commerce.
,, .	Dyera	costulata (Hook. *f.*)	*Malay Peninsula;* yields '*Jelutong*' of commerce.
Urticaceæ .	Ficus	elastica (Roxb.)	*Asia* (Burmah, Malaya, Java, India). Yields the '*Rambong*' of commerce. Has been planted to some extent in the Dutch and German colonies.
,, .	Castilloa	elastica (Cerv.); *Ulei* (Warb.)	*Mexico; Central America; Peru.* Planted to some extent in Mexico and German colonies, &c. Yield the '*Caucho,*' '*Mexican strips,*' '*Centrals,*' &c. of commerce.
Compositæ .	Parthenium	argentatum (A. Gray)	*Mexico; Texas* (*Guayule* of commerce).

coagulating vessels is compressed (*unsmoked*) into irregular masses, and goes by the name of *Negro-heads.* The Amazon territory at the present time supplies about one-half of the world's total output.

Plantation rubber. The tree which has been almost universally adopted on the eastern plantations (Malaya, Ceylon, S. India, Java, Sumatra, Borneo) is the *Hevea brasiliensis,* but the methods of collection and coagulation, &c., are markedly different from those employed on the Amazon. The trees are tapped mostly on the (half) herringbone system, which consists of a series of oblique cuts running into a central channel. The latex is collected in a cup connected with the central channel at the base of the tree. Tappings take place daily or on alternate days over certain periods, the tapping consisting in a paring away of a strip of bark of about $\frac{1}{20}$th to $\frac{1}{30}$th of an inch wide along each oblique incision. This is repeated until a certain area of bark has been removed. The portion of the tree so operated on is then allowed a period of rest sufficient for bark renewal, for which 3 to 4 years appears to be an appropriate period. Plantation latex is generally coagulated by the addition of a small quantity of acetic acid. After the coagulum is formed it is removed from the serum and passed through washing rolls, which squeeze out much of the remanent mother liquor and wash out the excess of non-rubber latex constituents. These rolls are of much the same construction as those used in the factory for *washing* (*see* below). The rubber is subsequently hung up to dry in the form of a sheet or crepe, and is frequently 'smoked' during the drying period, coco-nut husks and hard wood being employed for this purpose. Plantation rubber is invariably shipped bone-dry and is of a translucent light cream to amber colour for ordinary varieties to a dark amber in the case of the smoked goods. Dryness and cleanliness are the characteristics of plantation rubbers which differentiate them sharply from 'wild' descriptions. The production of plantation rubber in 1912 was about 25,000–30,000 tons; in 1910 it was approximately 8000 tons; ten years ago the quantity produced was altogether negligible.

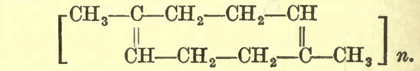
While plantation rubber is practically dry and clean, other crude rubbers of commerce contain varying quantities of moisture and mechanical impurities, such as sand, stones, bark, &c., and frequently an excessive amount of chemical 'impurities,' such as resin, proteid, decomposing animal and vegetable matter, &c. These rubbers must undergo a thorough process of cleansing before they can be used in the factory, and this process consists substantially in passing the rubber, after it has been cut up and steeped in warm water, through washing rolls, whereby it is subjected to a combined process of washing and disintegration. After 'washing' the rubber is dried, and the loss of weight which results from the washing and drying operations is termed 'washing loss.'

The following table shows the average 'washing loss' of a number of the more important commercial varieties:—

Commercial Name.	Washing Loss.
Fine Para (hard and soft cure) .	12–20 p.c.
Negro-heads	20–40 ,,
Matto Grosso	15–30 ,,
Maniçoba	28–30 ,,
Mangabeira	30–35 ,,
Congo varieties, better class, such as Upper Congo, Red and Black Kassai, Equateur, &c. . . .	6–12 ,,
African niggers (Soudan, Conakry Niger) and Gold Coast 'Lumps,' &c.	15–40 ,,
Assam	15–40 ,,

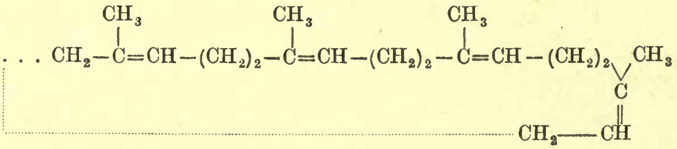
Nature of crude rubber. Washed commercial *crude* or *raw* rubber consists of 'caoutchouc' or rubber proper *plus* varying quantities of 'impurities,' of which the more important are the *resins* (substances soluble in acetone or alcohol, and, so far as they have been investigated, containing oxygen in varying proportions); *nitrogen* (partly as proteid), *mineral constituents* (principally lime, potash, and magnesium compounds), and *insoluble matter.* The latter in the case of *fine Para* (Spence) is of a fibrous character and contains a high proportion of nitrogen, possibly in the shape of a glyco-protein. It was formerly believed that rubber consisted substantially of two isomeric bodies, the 'adhesive' and the 'nervous' principles respectively, and that the insoluble matter was the 'nervous' moiety, but this certainly is not the case. Many well-prepared rubbers dissolve practically completely in ordinary rubber solvents, and, as Weber showed, the average proportion of 'insoluble' matter in dry fine Para is no more than 3–4 p.c. With regard to the quantities of resin, nitrogen, ash, &c., contained in commercial rubbers, there is a wide variation according to the method of collection, coagulation, and subsequent treatment, many of the 'native' or 'wild' rubbers being prepared in a very primitive manner, and arriving in a wet, sticky or dirty condition; but it may be stated that properly prepared plantation rubbers (*Hevea*) need not contain more than 2–3 p.c. of resin, 0·2–0·4 p.c. of nitrogen, very little insoluble matter (1–2 p.c.), and under 1 p.c. of ash. Fine Para grades generally contain slightly more nitrogen and insoluble matter than plantation grades, calculated in both cases to 'dry substance.' *Castilloa* and *Manihot* may be prepared to contain not more than 3–5 p.c. of resin, and suitable *Ficus*, *Funtumia*, and *Landolphia* species also yield rubbers not showing more than 5–7 p.c. All the rubbers referred to may be prepared to reach the market in a dry, clean condition, and containing roughly not more than 3–5 p.c. jointly of ash, proteid, and other non-rubber and non-resin constituents.

The rubber hydrocarbon. On highly purifying commercial rubber a material is obtained which approaches very closely to the composition demanded by the formula $(C_5H_8)n$ or $(C_{10}H_{16})n$. The balance of opinion appears to be favourable to the latter. With regard to the constitution of the molecule, Harries, on the basis of work on the fission products of rubber ozonides, regards it as 1·5 dimethyl-cyclo-octadien



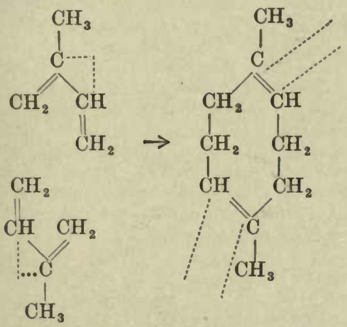
$$\left[\begin{array}{l} CH_3-C-CH_2-CH_2-CH \\ \qquad\ \ \| \qquad\qquad\qquad\quad \| \\ \qquad CH-CH_2-CH_2-C-CH_3 \end{array}\right] n.$$

The rubbers obtained from different genera are not, apparently, all identical in structure. Harries found that whereas the ozonides obtainable from purified *Hevea* gave on hydrolysis mainly lævulic aldehyde, with lævulic acid as a secondary product, the reverse was the case with ozonides obtained from gutta-percha and from certain African (*Landolphia* or *Funtumia*) species. The explanation offered is that the ozonide complex occupies a different position relatively to the plane of the eight-ring in space, a *cis*-position in the one, a *trans*-position in the other case. Pickles has suggested that the admitted chemical data regarding the behaviour of the rubber molecule may be best explained by assuming that it does not consist of a number of $C_{10}H_{16}$ rings polymerised to a complex molecule, but of a single ring containing a number of unsaturated C_5H_8 nuclei, *e.g.*:



$$\ldots CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-(CH_2)_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-(CH_2)_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-(CH_2)_2\!\!\underset{\displaystyle \overset{\|}{\underset{}{}} }{\overset{\vee}{C}}\!\!CH_3 \quad \ldots CH_2-CH$$

If rubber is submitted to dry distillation a number of isomeric hydrocarbons of the formula C_5H_8 are obtained, among these being *Dipentene* (b.p. 171°) and *Isoprene* (b.p. 37·5°) (*q.v.*). From the latter product a material which appears to be identical with rubber has been synthesised by numerous observers starting with Bouchardat (1875) and Tilden (1882). The polymerising agents which have from time to time been employed by different workers include hydrochloric acid, acetic acid and acetic anhydride. alkalis, metallic sodium and potassium, and various neutral salts. The operation of the polymerising agent has generally been assisted by heat and pressure. The mechanism of the condensation of isoprene to rubber may be explained as follows :—

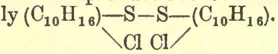


2 mols isoprene. Rubber nucleus.

The manufacture of *commercial synthetic rubber* will only be possible if a suitable low-priced raw material, capable of transformation at a low cost and with a high yield, can be found. So far these conditions do not appear to have been fulfilled.

Properties of crude rubber. Among the *derivatives* of rubber which are apparently of definite *chemical* composition may be mentioned the ozonide $C_{10}H_{16}(O_3)_2$, oxygen derivatives $C_{10}H_{16}O$ and $C_{10}H_{16}O_3$, the bromides $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_5$. the nitrosites $C_{10}H_{16}N_3O_3$, $(C_{10}H_{15}N_3O_8)_2$, $(C_{10}H_{15}N_3O_7)_2$, and $C_{40}H_{62}N_{10}O_{24}$ and the nitrosates $C_{10}H_{12}N_2O_6$ and $C_{10}H_{16}N_2O_4$. For sulphur derivatives *cf.* below under *Vulcanisation.*

Physical properties. Like most colloids rubber is not (as was generally believed formerly) a structureless mass, but possesses a certain structure varying with the method of preparation and treatment. Freshly coagulated rubber shows reticular structure, the 'net' being composed of the globules originally present in the latex. The globular particles persist even after the rubber has been dried and are visible in rubber solutions made from dried rubber. Films prepared from solutions no longer display reticular structure under ordinary circumstances, but a pronounced network is formed if such films are subjected to the action of diluted sulphur chloride (*cold vulcanised*). The *specific gravity* of clean commercial rubber is about 0·91. On warming the material, the specific gravity gradually decreases and the material becomes soft, then sticky, and finally 'melts.' If crude rubber is cooled it hardens appreciably at temperatures below (about) 50°F., and at (about) 35°–40°F. becomes quite hard and entirely loses its elasticity. Rubber that has been stretched contracts on warming, and heat is absorbed. At ordinary temperatures freshly-cut surfaces of crude rubber adhere to one another. Vulcanised rubber does not appreciably harden or soften on exposure to moderate cold or heat, and is not adhesive. Vulcanisation also improves the mechanical properties of rubber (strength, elasticity, resilience). The physical properties of crude rubber are indeed such that, but for the discovery of the process of vulcanisation, the industry could never have attained to more than very moderate proportions. Like most organic gels crude rubber absorbs water freely, increasing thereby some 25 p.c. in weight and 15 p.c. in volume. With petroleum and coal-tar hydrocarbons, carbon disulphide, with many chlorine derivatives of methane, ethane, and ethylene, and with essential oils it forms typical colloidal solutions. The most important technical solvents are 'solvent naphtha' (coal tar and shale) and carbon disulphide. Rubber solutions are extremely viscous, but the degree of viscosity depends largely on the nature of the rubber and on its treatment previous to exposure to the solvent. Mechanical working greatly increases the solubility but decreases the viscosity of crude rubber. For manufacturing 'solution' required for spreading, particularly where great strength and covering power are required, the less the material is worked, therefore, the better. Where a solution is required for cementing and sticking objects together, a certain amount of 'working' is desirable, as adhesion is thereby, up to a certain point, increased. There appears to be a distinct connection between the viscosity of a rubber solution and the strength of the material, and this relationship may be utilised in comparing different samples of rubber of the same species. *Dry* crude rubber is a fairly good non-conductor of electricity and is used to a considerable extent as an inner lapping (next to the wires) in conjunction with an outer lapping of vulcanised rubber, in electric light and power cables and 'flexibles.'

Vulcanisation. The application of heat to a mixture of rubber and sulphur effects a profound change in the character of the raw material (*see* above). The process of vulcanisation, as this process is termed, is not accompanied by the evolution of any appreciable quantity of sulphuretted hydrogen, and the reaction, therefore, must be either physical (*i.e. adsorption*), or, if chemical, of a purely additive character. Recent research by Spence, which to some extent is confirmed by the work of the author, supports the view that the process is mainly a chemical one, and only in a very minor degree of an adsorptive character. According to Weber the effects of vulcanisation are not distinctive until the vulcanised material contains 2–2·5 p.c. of combined sulphur (*i.e.* sulphur not removable by solvents or other physical means); this would correspond roughly to $(C_{10}H_{16})_{10}S_2$, and specimens of ebonite (the product obtained if vulcanisation is carried to the ultimate practical limit by means of large quantities of sulphur, prolonged time and high temperatures) prepared with 50, 75, and 100 p.c. of sulphur respectively all yielded products containing approximately 32 p.c. of combined sulphur, corresponding roughly to $C_{10}H_{16}S_2$. Weber concluded that there is a series of products between these extremes, but later work casts serious doubts on the accuracy of these deductions. It is, however, the fact that the amount of combined sulphur stands in some direct relationship, if not ratio, to the amount of sulphur employed and to the time and temperature of the operation. With increasing sulphur, time and temperature, the material after a certain period becomes gradually harder (*i.e.* increases in tensile strength) and decreases in elasticity. Broadly speaking, normal soft rubbers contain 3–4 p.c. of combined sulphur, hard rubber or ebonite 20–30 p.c. An effect similar to that produced by the combined action of sulphur and heat on rubber (*i.e.* the *hot cure*) is obtained by allowing a diluted (3–5 p.c.) of S_2Cl_2 in CS_2 to act on the material. This process, which, owing to the extremely active nature of the reagent employed, can only be employed for vulcanising very thin goods—for if applied to massive articles the exterior would be much over-cured by the time the solution had penetrated to and adequately vulcanised the interior—is called *cold curing* or cold vulcanising, and is accompanied by the binding of sulphur and chlorine, apparently in the same relative proportions as these elements exist in S_2Cl_2. The end product of the reaction is not improbably  $(C_{10}H_{16})—\underset{\diagdown Cl}{S}—\underset{Cl\diagup}{S}—(C_{10}H_{16})$. Hinrichsen advances the theory that ordinary 'cold-cured' goods consist of solid or semi-solid solutions of this 'end product' in rubber, *plus* varying quantities of adsorbed 'free' sulphur.

The rubber industry proper is of comparatively recent origin. In 1830 no more than 23 tons of the crude material were imported into the United Kingdom; in 1850, 381 tons; in 1870, 7656 tons. In 1910 the figure reached was as high as 43,848 tons. The writer estimates the total production of raw rubber in 1911 to be between 86,000–93,000 tons, of which rather less than one-half will come from the Amazon districts, 15,000 tons from the Eastern plantations, 15,000–17,000 tons from Africa, and a similar quantity from Mexico, Central America, &c. The United States consume about one-half of the world's output, the United Kingdom and Germany each about one-sixth, and other countries the remaining one-sixth. Production, principally owing to the development of the Eastern plantations, is rapidly increasing, and it is estimated that in 1915–1916 the total raw rubber output will not be far short of 150,000 tons.

While, as stated, the rubber industry proper is of recent origin, the first known reference to the raw material in European literature dates back to 1525, in which year P. Martyr d'Anghiera published a description of some rubber playing balls seen by him in Mexico. It is clear from the records, principally of Spanish and Portuguese writers, that the natives of rubber-bearing districts have for many centuries past recognised the valuable properties of raw rubber, and have made therefrom articles such as playing balls, pouches, boots, and 'waterproof' garments. About 1770 Priestley (the discoverer of oxygen) recommended the use of the material (which at that time was obviously imported from the West Indies) for erasing pencil marks, hence the name 'India-rubber,' and in 1763 Herissant and Macquer sent a memoir dealing with the behaviour of the material towards various solvents to the Paris Academy of Sciences. The latter appears to be the earliest scientific paper on rubber on record. Serious attempts to make use of rubber industrially do not appear to have been made until the beginning of the 19th century. A process, patented by Samuel Peal in 1791 for waterproofing cloth by spreading it (by hand) did not meet with much success, but about 1825, Charles Macintosh of Manchester, having discovered that rubber is soluble in coal tar naphtha, produced 'proofed' garments by a practicable process, and this may be regarded as the starting-point of the modern rubber industry. Nevertheless, it was not until after the process of vulcanisation was discovered by Charles Goodyear of Newhaven, U.S.A., in 1839, and independently by Thomas Hancock of London in 1844, that it showed signs of becoming of first-rate importance. Goodyear mixed masticated crude rubber with finely divided sulphur, and on heating the mass observed the characteristic modification of the properties of the raw material mentioned above. Hancock (who was unaware of Goodyear's work) observed that similar results were obtained by dipping crude rubber into melted sulphur. In 1846 Parkes discovered the process of cold vulcanisation. Among the earlier inventions may be mentioned that of a masticating machine and process by Hancock, which made the manufacture of rubber sheet a practicable operation and much facilitated the production of 'solution.'

Manufacture of rubber goods. Raw rubber, if we except the best plantation grades, always contains more or less foreign matter (sand, dirt, bark, moisture, soluble proteids, &c.) which must be eliminated before it can be used for manufacturing purposes. The process of removing the impurities referred to is termed '*washing.*' The rubber having been cut into lumps or slabs is first steeped for some hours in warm water to render it pliable and to remove some of the soluble impurities, and is then passed through the washing rollers (Fig. 1). The rolls are corrugated, diamond cut or fluted, and run at a differential speed varying from 6 : 4 to one tooth difference. While many washing machines are still belt driven, modern practice favours direct electric drive wherever this is possible. Fig. 1 shows a modern machine of this type by David Bridge & Co. A stream of water is kept running upon the rubber during the whole of the operation. The pieces of rubber passing through the rollers are converted by the combined squeezing and disintegrating action of the latter into a rough corrugated sheet. This sheet, which is of a crepe-like texture, is repeatedly passed through the rolls until it is considered to be sufficiently clean and thin. It is then taken to the drying-room, where it is hung on racks until the moisture content has been reduced to approximately 0·25–0·5 p.c. Very low grade, resinous rubbers cannot be dried on racks, but are laid on canvas-covered frames, beneath and through which the air can circulate. Drying rooms are generally heated by means of steam pipes, but the best system is that of passing a current of warm air in a systematic manner through a series of drying chambers. The cooler (relatively) and drier the air the better, for the lower the temperature the less the rubber is inclined to become soft or 'tacky.' At a temperature of about 80°F. most factory-washed rubber can be dried in about 3–4 days if the conditions of ventilation are suitable. When dry the rubber is ready for *mastication* (if to be used for cut sheet, certain grades of thread or 'solution') or for *mixing*, if it is to be manufactured into other classes of goods. As the latter constitute by far the most important branch of rubber manufacture they will be considered first.

Mixing is the term applied to the operation by which sulphur and other materials are incorporated with the rubber. Very few articles are made from rubber and sulphur only, firstly, because of the prohibitive price; and secondly, because 'pure' rubber mixings, on account of their softness and great elasticity, &c., are unsuitable for the majority of commercial goods. The materials, other than rubber and sulphur, employed in commercial mixings may be broadly classified—there is necessarily much overlapping—as follows:—

(1) *'Fillers' or 'cheapeners' pure and simple*, comprising such substances as powdered chalk, barytes, ground rubber waste, 'oil substitute,' 'reclaimed' rubber, zinc oxide, &c.

(2) *Materials used for specific purposes.* (a) *For increasing mechanical strength, i.e.* for hardening or toughening goods, zinc oxide, lithopone, magnesia (oxide and carbonate) lime, litharge, ground glass, balata, &c.

(b) *For obtaining dense, non-porous mixings* (*i.e.* resistance to water, improvement of dielectric properties), asphalt, bitumen, pitch, ozokerite, &c.

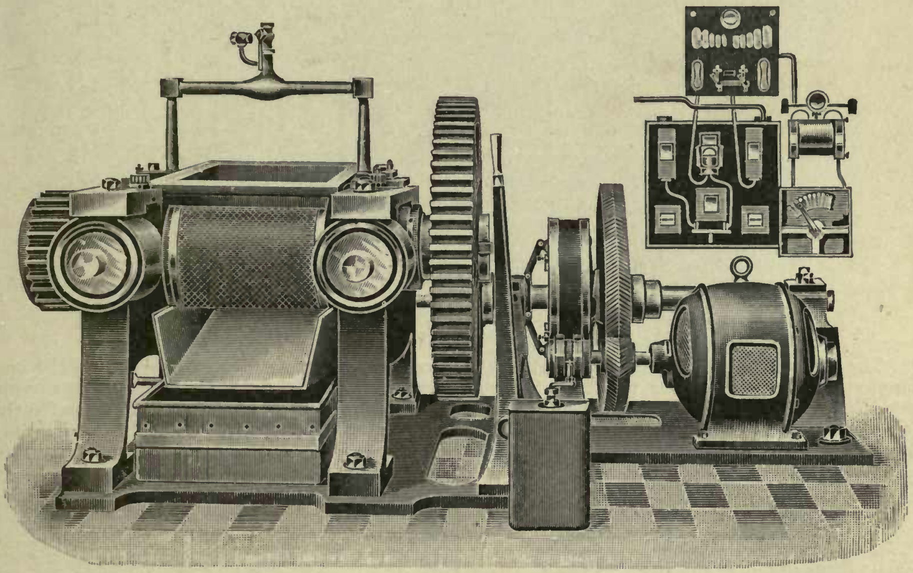


FIG. 1.

(c) *For improving vulcanising conditions*, litharge, magnesia, quicklime, antimony sulphide (*cf.* below under *Vulcanisation*).

(3) *Pigments*, such as zinc oxide, lithopone, zinc sulphide, antimony sulphide ('golden' and 'crimson sulphide'), mercuric sulphide (*vermilion, cinnabar*), cadmium yellow, chrome yellow, chrome green, prussian blue, &c., and various metallic powders used as 'lustres' or 'bronzes.'

'Oil substitutes,' obtained by the action of either S_2Cl_2 in the cold (white substitute) or of sulphur and heat (brown substitute) on colza, rape, maize, and other vegetable oils, are generally employed with a view to reducing the specific gravity of low grade goods.

Reclaimed rubber (*cf.* below under *Waste rubber*) is very useful in the production of moderate priced mixings, particularly in those cases in which large quantities of 'minerals' cannot be employed.

Fig. 2 shows a mixing machine, which, in general construction, is similar to the 'washer.' The smooth rolls, which run at different speeds, are hollow and fitted with the necessary connections for heating by steam or cooling with water. Any material falling through the rolls during mixing is caught in a metal tray sustained by appropriate stays. For the purpose of facilitating the removal of sticky mixings from the rolls a 'doctor' (actuated, *cf.* illustration, by gear B) is fitted to the rear roll. The first operation in mixing is that of 'breaking down,' *i.e.* of plasticising the rubber, which is achieved by passing the material repeatedly through the hot rolls, and gradually tightening up the latter. When the rubber is in a thoroughly plastic condition the other materials (reclaimed rubber, ground waste, 'substitute,' other organic fillers, and finally minerals and sulphur) of the mixing are gradually added. The aim of the mixer should be to obtain a thoroughly homogeneous dough without overworking or 'tiring' the rubber. In the case of the manufacture of the vast majority of 'mechanicals,' the dough or compound, while still warm from the mixing operations, is passed through a calender with a view to obtaining the material in homogeneous sheet form of a given thickness. Most calenders consist of a set of three superimposed, steam-heated, very heavy rolls, generally fitted with a change gear so that they may operate either at even or friction speeds (the latter for coating fabrics, the former for producing ordinary sheet). Fig. 3 demonstrates in diagrammatic form the operations of a three-bowl calender. The rubber dough, R, passes between the bowls A and B, and thence between B and C, as indicated. The homogeneous sheet so formed is carried forward by a coarse cloth unwound from roller E. The calendered sheet together with the canvas is rolled upon roller D. The object of using the cloth is to prevent the various layers of rubber from sticking to one another. Calendered sheet or rough 'compound' should be allowed a period of rest before it is vulcanised, so that it may recover from the somewhat strenuous mixing operation.

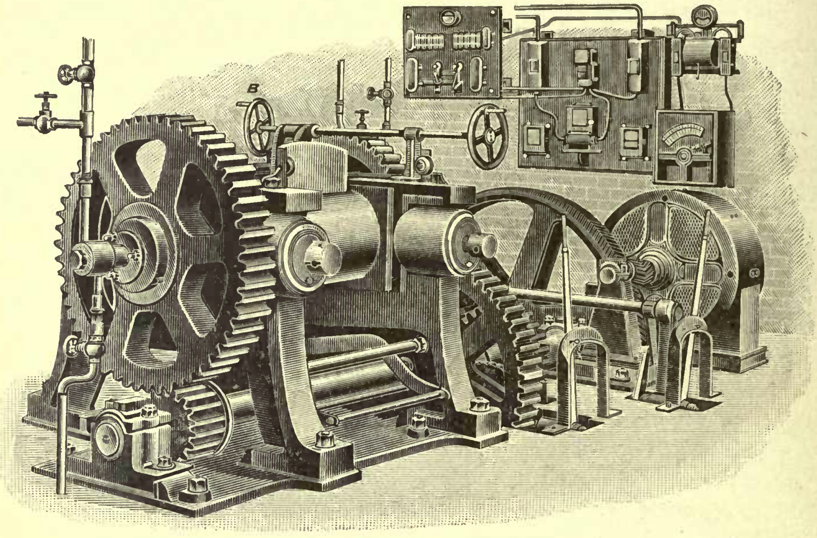


Fig. 2.

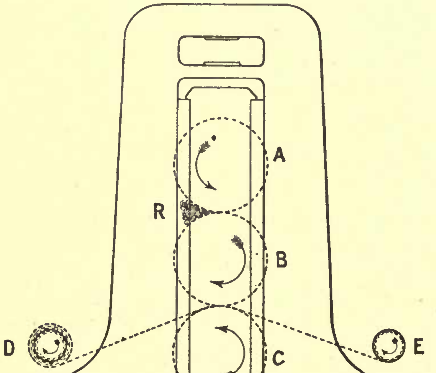


Fig. 3.

Vulcanisation. A. *Hot process.*—According to the class of goods to be made, the 'curing' takes place either in live steam (*open* or *steam cure*), in the vulcanising (generally *hydraulic*) press or in hot air (*dry heat cure*). In the *live steam cure* the articles are either cured in moulds (*e.g.* valves, buffers, tyre covers, &c.), or tightly wrapped with canvas (*e.g.* hose of various kinds) or simply imbedded in a thick layer of French chalk. Fig. 4 is a representation of a live steam vulcaniser. These vessels are made of very large size, up to 80 ft. in length and 6 ft. in breadth. In modern practice it is very usual to have a steam jacket fitted to the live cure vessel, a very material equalisation of temperature being brought about in this way. For all practical purposes, then, the live cure vessel is a large autoclave, working with steam and with the usual fittings for control of temperature and pressure, &c. The ordinary vulcanising heats lie between 135° and 145°C.

Press curing. Fig. 5 is an illustration of a modern hydraulic vulcanising press by Messrs. D. Bridge & Co. The goods, either in moulds, or in the case of sheet built up in a frame, are placed between the hollow steam-heated plates of the press, and pressure is then applied. There is no doubt that the greater the pressure during curing, the better the results, and in this respect the press has a great advantage over the live cure. Other advantages of the press are that relatively large articles of a homogeneous character (*e.g.* sheet) may be economically turned out, and that the pressure can be regulated independently of the temperature. On the other hand, *cæteris paribus*, goods cure much more rapidly in live steam than in the press, and it is a somewhat difficult task to maintain the different plates of the press at the same temperature, some unevenness between the lower and upper surfaces of the goods frequently resulting. It is possible to combine the advantages of the live steam cure with those of the press cure by means of the *autoclave press* (*pan-press*). This, in principle, consists of an hydraulic press, the working parts of which are enclosed in an air-tight jacket or chamber to which steam is admitted. For certain classes of goods, *e.g.* tyre covers, the pan press is used to a very considerable extent in modern practice.

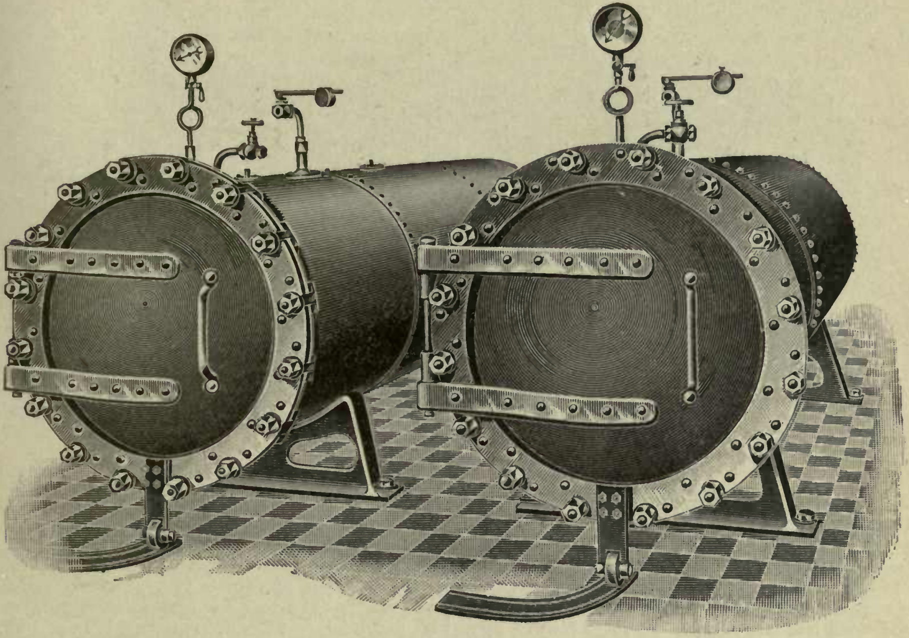


FIG. 4.

Hot-air (*dry heat*) *cure.* This, also known as the Waddington process, is frequently employed, *inter alia*, for curing proofed textiles which were formerly 'cold cured.' The cloth, on to which an appropriate dough of rubber, sulphur, &c. has been frictioned or spread (*see* below), passes over a series of rollers contained in a closed chamber heated by means of a steam jacket or coils. The time and heat are regulated so that the material may be perfectly cured during the passage through the 'stove.' The dry heat cure is particularly useful for vulcanising goods the appearance or properties of which (*e.g.* goloshes or shoes) would be damaged by steam.

B. *Cold process.* 'Cold curing' consists, substantially, in exposing a thin layer of rubber (either as such, *e.g.* in the case of 'cut sheet,' or frictioned or spread on a fabric) to the action of a 2 to 3 p.c. solutions of S_2Cl_2 in CS_2. With the exception of the types of goods cured by 'dry-heat,' practically all proofed garments and fabrics are cold cured. The first operation of cold curing consists in the manufacture of the dough. For this purpose a mixing consisting of rubber only, or of rubber with minerals, pigments, &c., *but without sulphur*, is made in the ordinary way on the mixing rolls, and after rolling out to a thin sheet, is exposed to the action of solvent naphtha in a zinc-lined vessel. In some cases the dough and solvent are worked together by means of rollers. According to the type of 'dough' required more or less of the solvent is employed. After the immersed sheet has absorbed sufficient solvent, it is passed through the 'dough rollers' which run at equal speed and have as their object the production of a mass thoroughly homogeneous in composition. When the solvent and mixing have been thoroughly incorporated the dough is ready for the next operation, viz. that of 'spreading' (*cf.*

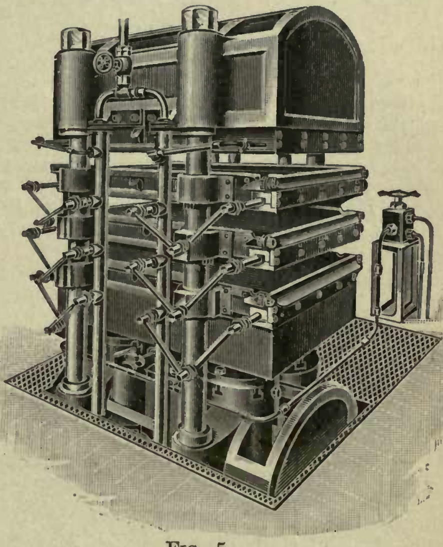


FIG. 5.

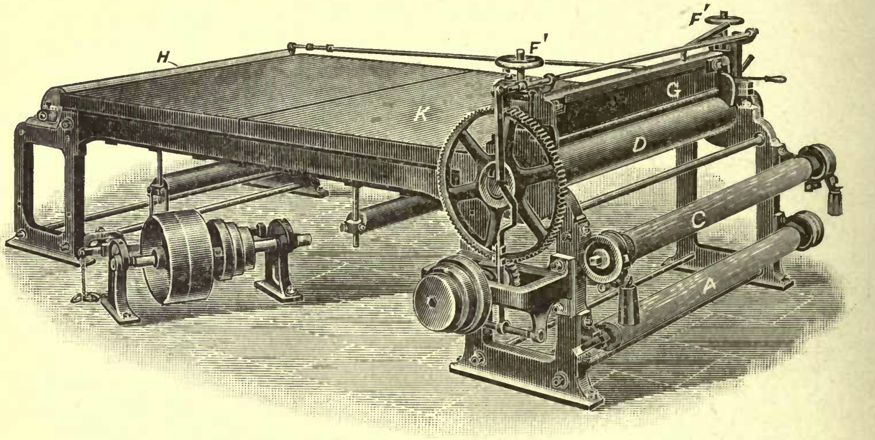


Fig. 6.

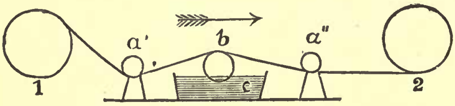


Fig. 7.

Fig. 6). The fabric to be coated is placed on roller A, attached to a piece of calico or other cloth, and the latter carried over the roller B, under the knife or 'doctor' G, over table K, and then wrapped round roller H. The dough is placed in the shape of a thick roll or mass upon the fabric between the guides and resting upon the roller D, and against the 'doctor' G. The height, or rather pressure, of the latter (regulated by means of F, F′) above the cloth determines the thickness of the layer of dough spread on the cloth as it passes beneath G. After the cloth has had a layer of dough spread upon it in the manner indicated it passes along the steam-heated chest or table K, the result being that by the time it reaches the 'taking-up' roller H, the solvent has evaporated off. In the majority of cases a number of coats of 'dough' are applied successively, even very thinly spread textures frequently having 15–20 coats applied. The fabrics employed vary a good deal according to the prevailing fashions and are generally specially made for the proofing industry. Fabrics with rubber on one side and cloth on the other are termed 'single texture'; where a layer of rubber is contained between two surfaces of fabric, the term 'double texture' is employed. After 'spreading' has taken place the goods are cured (*i.e.* vulcanised), the sulphur chloride solution being contained in a lead lined wooden trough. Fig. 7 shows diagrammatically the method of procedure. The goods travel from roller 1 to 2 as indicated, the vulcanising solution in C being applied by means of roller *b*. By the time the goods arrive at roller 2 they are sufficiently cured and dry to roll up. For making 'double textures' the two cloths travel towards one another, and after being cured in separate baths pass through the doubling rollers together before vulcanisation has completely taken place. The method of attaining this result is evident from Fig. 8, in which E and D are the doubling rollers diagrammatically presented. The latter it may be added are also used for uniting fabrics spread with

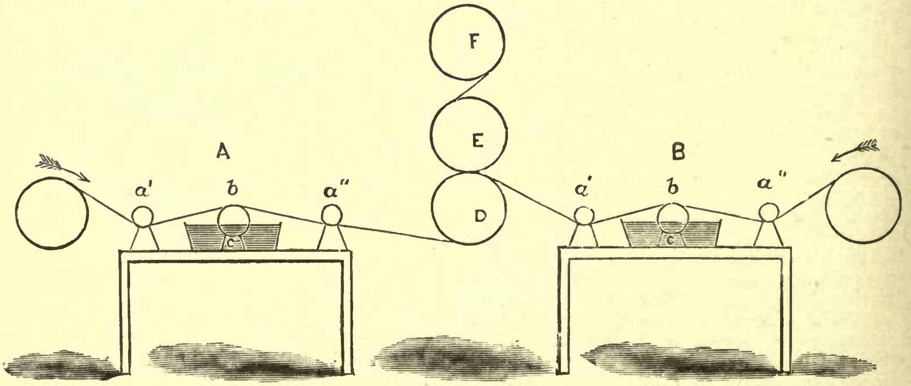


Fig. 8.

doughs containing sulphur, which are subsequently cured in steam or by dry heat and also for doubling calendered sheet.

Manufacture of Various Classes of Goods.

Cut sheet, which is employed for tobacco-pouches, surgical goods, and similar articles is, or should be, made from the highest grade of materials only. The washed rubber is first masticated in a machine such as in shown in Fig. 9, the essential feature of which (Fig. 10) is a fluted roller B, whereby the rubber (C) is converted into a homogeneous, masticated dough. The hot mass is then compressed by hydraulic power into cylindrical or oblong block moulds, and after the solid blocks of rubber have been removed from the moulds they are frozen until quite hard. As a rule refrigerating chambers are employed for this purpose nowadays. The frozen blocks are now cut either into sheets or to a continuous band by means of rapidly oscillating knives. Fig. 11 illustrates a cutting machine for making rectangular sheets. The carriage travels to and fro, and after a sheet has been cut off, the block is raised through a height equal to the thickness of the sheet, preparatory to cutting the next section. Cut sheet goods are generally cold cured, but certain articles, for instance, feeding teats, are vulcanised by immersion in a sulphur-bath. The cut-sheet trade, partly owing to the expense of manufacture and partly to the improved quality of 'rolled' sheet obtainable by modern calender work, appears to be a declining one.

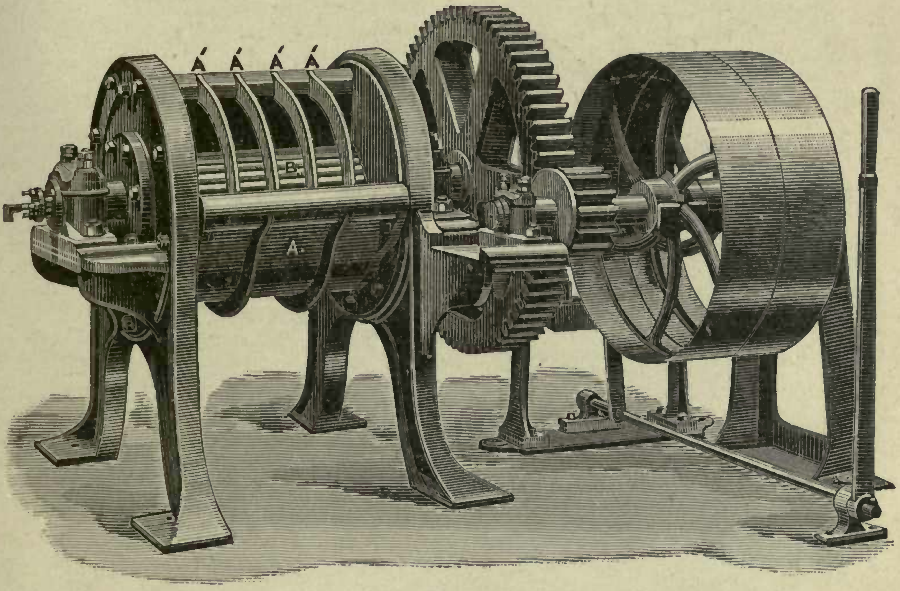


Fig. 9.

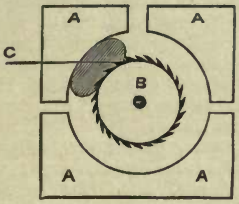


Fig. 10.

Elastic thread is mainly employed in the manufacture of 'webbings' (braces, garters, 'spring-side' boots, surgical appliances, &c.) and for winding the cores of golf balls. It is made either by spreading or by calendering. In the manufacture of 'spread-thread' a number of coatings of a dough consisting (in the case of the best qualities) substantially of rubber, sulphur, and naphtha are spread or frictioned on to sized calico or on to cloth having a coating of vulcanised rubber as a foundation. The rubber layer is then dusted with French chalk (to prevent adhesion after stripping), stripped from the cloth, made true at the edges, interlined with cloth, and wound upon a drum. The whole is tightly wrapped in cloth and then vulcanised in live steam. When the cure is finished the rubber sheet is removed from the drum, pasted over with a strong solution of shellac in methylated spirit, and while still wet wound upon a roller (which has a foundation of rubber about a quarter of an inch thick to preserve the thread cutting knife from damage) so as to form a cylinder, which dries to a compact block. The rubber is then placed in a cutting lathe and the thread cut to the desired gauge. The final operation consists in removing excess of sulphur and shellac by boiling in a solution of caustic soda. 'Calendered-thread' is made in a manner very similar to 'spread-thread,' the essential difference being that the manufacturer starts with calendered instead of spread sheet.

Tyres. *Solid tyres* (cab tyres, omnibus tyres, rickshaw tyres, &c.) are generally made by 'squirting' an appropriate mixing through a die in the forcing machine, of which Fig. 12 is a diagrammatic representation. The dough is fed through hopper A into a steam-jacketed chamber in which it is carried forward to the nose-piece C (in which the die is fitted) by means of the screw B. As the tyre emerges from the machine it is coiled on a tray containing French chalk, and is subsequently vulcanised in open steam or hot air. Special kinds of solid tyres are also cured in moulds, but this method is relatively expensive.

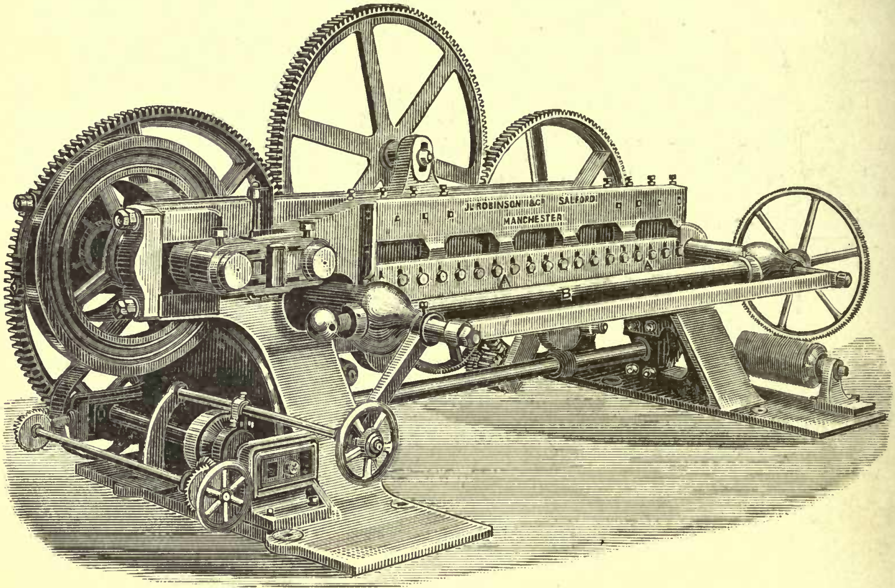


Fig. 11.

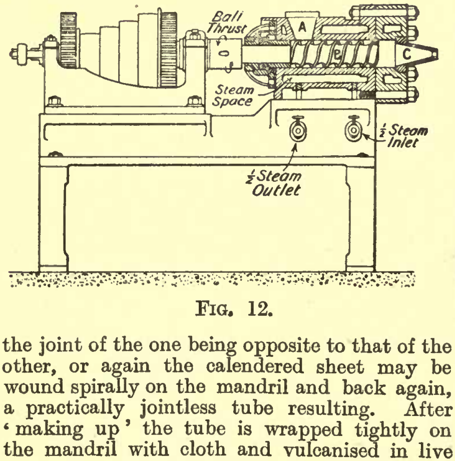


Fig. 12.

Pneumatic tyres. Inner tubes are generally made from calendered sheet, although very good results are obtained by some makers by 'squirting.' When calendered sheet is employed it is cut to the desired length and lapped round a mandril, the join being made by means of a slip of rubber and rubber solution. Another method consists in building up from two pieces, the joint of the one being opposite to that of the other, or again the calendered sheet may be wound spirally on the mandril and back again, a practically jointless tube resulting. After 'making up' the tube is wrapped tightly on the mandril with cloth and vulcanised in live steam. Subsequently the tube is removed from the mandril and the ends joined up by means of 'solution,' and a cold curing process, or by some equally appropriate method. Occasionally tubes are cured in moulds, the collapse of the tube being prevented by the introduction, prior to curing, of an adequate amount of ammonia or ammonium-carbonate between the walls. This principle is also employed in the manufacture of playing balls and other hollow articles. Pneumatic tyre *covers* are built up on the mandril, mostly by hand, from layers of proofed canvas and calendered sheet. Vulcanisation of covers is generally carried out in moulds, but occasionally they are mechanically 'wrapped' and then cured in open steam.

Hose of better grades such as pressure hose (*e.g. for liquids*: fire-brigade hose, for pumping, for brewers' use, &c.; for *steam*: railway couplings and breaks, &c.) and vacuum hose (*e.g.* for vacuum brakes, for mining work, &c.) are generally built up from calendered sheet, proofed canvas, and other fabrics, with and without metallic strengthening insertions such as wire, metal bands, &c. Most varieties are made in considerable lengths—the usual 'standard' size is 60 ft.—but special kinds, such as railway vacuum hose, are made up in short lengths, generally by hand. A number of mechanical appliances are used in making up various grades. Thus ordinary 'friction' hose may be made (*a*) by lapping alternate layers of calendered sheet and canvas round a long mandril horizontally disposed in a hose-making or wrapping machine; (*b*) by drawing a seamless inner tube over the mandril and then lapping or wrapping on canvas; (*c*) by drawing a seamless ('squirted') tube simultaneously with a canvas strip through a machine which folds the latter over the tube; (*d*) by spinning a yarn on to lapped sheet or seamless tube.

Buffers, valves, &c. Simple buffers ('buffer-springs') are made by vulcanising in moulds calendered sheet which has been lapped round a mandril until the requisite thickness is obtained. In some cases the goods are separately fashioned prior to curing, in others the finished article is obtained by cutting a section of the required thickness from the vulcanised cylinder.

Belting. A suitable dough is spread or frictioned on to both sides of strong proofed canvas, and after the latter has been cut into strips, a number of the latter are built up until the requisite thickness is obtained. Such belts are vulcanised in long hydraulic presses.

Heels and *heel pads* and many other small articles are stamped from calendered sheet and subsequently vulcanised in moulds.

Rings are either made by 'solutioning' together tape or cord, or by cutting from a tube in the lathe.

Tubing is either 'squirted' or built up by pressing together the bevelled edges of calendered sheet cut to the requisite width.

Ebonite, vulcanite, or hard rubber is the product obtained by vulcanising for a prolonged period (*e.g.* for 6 hours as against 2 hours for soft goods) a mixing containing a high proportion (*e.g.* 25–40 p.c. as against 5–10 p.c. for soft goods) of sulphur. Except when mixed with pigments 'hard rubber' is a material of an ebony-black colour, relatively hard and inelastic and yet—if of good quality—capable of being bent to a considerable degree without breaking. It will take a high polish and may be turned, and, after softening by heat, moulded and pressed. The better grades (*i.e.* those made from rubber, sulphur, and high-class ebonite dust only) are very indifferent towards chemical reagents such as acids and alkalis, and on this account they are largely employed in chemical factories (pumps, pipes, acid cocks, acid resisting coverings, &c.), for accumulator cases, &c. The ebonite 'mixing' is prepared in substantially the same way as that used for soft rubber goods, but great care must be taken to use materials absolutely free from sand, grit, and similar impurities, and the mixing must be of a very thorough nature. Sheet ebonite is generally, with a view to obtaining a good surface, covered with tinfoil prior to curing, the latter operation taking place in the water-bath between cast-iron plates. Moulded ebonite goods of high grade are cured either in glass or in metal covered with some material possessing an absolutely smooth surface.

Waste rubber. Many thousands of tons of waste rubber are collected annually, the better grades (*e.g.* motor inner tubes and good 'cold-cured' scrap) fetching relatively high prices. The bulk of it is employed, (*a*) after washing and grinding, as a filler in medium to low grade mixings, (*b*) as a basis for the manufacture of 'reclaimed' rubber, (*c*) for the purpose of making 'reformed' articles. The various processes used in the manufacture of *reclaimed* rubber consist substantially of a series of preliminary operations designed to remove all dirt, fibre, metal particles, &c., from the material, followed by treatment under varying conditions with chemical agents such as alkalis, acids, sulphites, &c., with a view to removal of as much as possible of the free sulphur and other non-rubber constituents. While it has been recently stated that 'reclaimed' from which substantially the whole of the combined—as well as the free—sulphur has been removed, is being manufactured, the writer has not yet come across an article of this nature. Goods of excellent quality are also produced by the so-called *reforming* process, which consists broadly, in the application of heat and pressure to powdered or flaked scrap in a mould.

PROPERTIES OF VULCANISED RUBBER.

It will be obvious that vulcanised rubbers must vary enormously *inter se* in their properties, according to the nature of the mixings employed, the methods of 'curing,' &c. Practically all grades, however, are gradually affected by the action of air and light, becoming hard, and finally brittle, but the effect is particularly rapid (*a*) in improperly cured goods, particularly if there is an excess of free sulphur; (*b*) in goods containing a large quantity of mineral fillers and 'reclaimed' or waste rubber. This hardening may be due either to (*a*) 'after vulcanisation,' or to (*b*) oxidation, or both, but whereas 'after-vulcanisation' is favoured by storage in a warm, dry atmosphere, exposure to light causes, particularly at higher temperatures, rapid oxidation. The oxidation of rubber results in the formation of resinous compounds of which certainly one is soluble in resin solvents, such as acetone or alcohol (Spiller's resin), the other (Burghardt's resin) insoluble. Besides light, air, and (particularly *dry*) heat, rubber is also seriously affected by even slight traces of copper and by vegetable and mineral oils. The effect of these agents appears to be chiefly that of hastening oxidation, but oils have a solvent action as well. According to Bing the hardening of rubber is always accompanied by the formation of traces of free sulphuric acid. Strong sulphuric and nitric acids rapidly attack even high grade soft rubbers, but towards dilute acids they are relatively stable; but, naturally, mixings containing soluble substances such as zinc oxide, magnesia, calcium carbonate, &c., will be affected according to the quantity of these and the nature, strength, and temperature of the acid in question. High-grade mixings are very stable towards alkalis, but in this case also the presence of substances soluble in or chemically modifiable by the reagent (*e.g.* zinc oxide, antimony sulphide, saponifiable matter, &c.) will cause the goods to be affected.

Physical properties. Compared with crude rubber, vulcanised rubber is relatively insensitive to changes of temperature. It is relatively impermeable to water and gases, and on this account, as is well known, is largely used in waterproofing, electrical, and balloon industries. Mixings composed of rubber and sulphur only are not the most suitable for resisting water, small quantities of such materials as bitumen, pitch, ozokerite, &c., causing an improvement from this point of view. 'Pure' mixings (v. Henri) are also more susceptible to attack by the actinic rays than articles prepared with suitable mineral fillers, and in the same way crude rubber is more susceptible than the vulcanised article. Rubber is an excellent electrical insulator, and in the soft form is largely used for lighting and power cables and 'flexibles,' and as ebonite for switch-boards, transformer tubes, and so on. High-class cables and flexibles are generally made with a lapping of crude rubber next to the wire, and this is covered with vulcanised strip, the object being to prevent the action of the sulphur in the latter on the conductor. For submarine cables rubber is very little used (excepting for shore end connections running through very shallow water), the main reasons being (*a*) the difficulty of making satisfactory joints (*b*) the relatively—as compared with the best gutta-percha—unsatisfactory resistance to water at high pressure, (*c*) the difficulty of entirely preventing any action of the sulphur on the conductor.

Mechanical properties. Rubber as an industrial material is chiefly valued on account of its mechanical properties. These will, naturally, vary with the nature of the mixing and cure, but within reasonable limits high-grade soft rubbers conform to certain general laws in a manner indicating the predominant and specific influence of the basis material. These laws—so far as they apply to tensile properties—formed the subject of a lucid research by Stévart, and briefly stated are as follows: (*a*) the effect of the load is inversely proportional to the cross-sectional area; (*b*) the total extensibility (*i.e.* elongation at break) is independent of the cross-sectional area; (*c*) extensibility is not directly proportional to the load, but increases with equal increments of load to a maximum and then decreases. This maximum is independent of the cross-sectional area, and for high-grade soft rubbers lies very close to the point at which the material has been extended to double its original length; (*d*) the relation between extension and load is of a complicated nature, the curve by which it may be expressed being probably of a higher order than the third power; (*e*) the load necessary to produce a specific extension is proportional to the cross-sectional area; (*f*) the modulus of elasticity of rubber is a varying, and not (as with metals) a constant quantity; (*g*) the maximum distensibility is accurately represented by the formula $e = x\frac{lo}{ES}$, where x is a constant dependent on the quality of the rubber, *lo* the original length of the test strip, E the mean value of the modulus of elasticity, and S the cross-sectional area. Perhaps the most characteristic feature of soft rubber curves is the inversion of sine at a point corresponding roughly to an extension of the material to twice its original length. It is also highly characteristic of good soft rubbers that as the breaking-point is approached the resistance to extension rapidly increases, or, in other words, the curve flattens rapidly, and the extension for an equal increment of load rapidly diminishes. Poor rubbers, *i.e.* those containing large quantities of mineral or other fillers, do not display these characteristic features; on the contrary, they behave much as do metals or other rigid materials; there is no reversal of sine and the resistance to tension decreases rapidly as the breaking-point is neared. Rubbers which have been undercured exhibit a relatively high extensibility and low breaking strain, over-cured rubbers (*coeteris paribus*) the reverse. When both extensibility and breaking strain are low, the presence of a considerable proportion of low-grade rubber or of non-mineral fillers (*i.e.* waste or reclaimed rubber, &c.) is indicated. Where the extensibility and 'combined' sulphur content are high, but the strength poor, the cause may be the overworking of the rubber on the rolls. Soft rubbers of good to high class should possess a breaking strain of 1000–2500 lbs. per square inch, and an elongation at break (taking the original length as=1) of 8–10. Medium soft to hardish rubbers of the same grades should break at 1200–3000 lbs., and exhibit an elongation of 6–8.

Compression. Rubber is practically incompressible, the figures obtained by different authorities being substantially of the same order as those for water. The volume of a mass of rubber, therefore, remains constant, whatever deformation it may undergo.

Hysteresis. If a strip of rubber is stressed to a point short of the break and the load is then removed, it will not return absolutely to its original length, but, according to the nature of the mixing and load applied, will show a certain amount of 'set.' That is to say, the retraction curve will not coincide with the elongation curve, the two forming a loop. This effect has been termed ***hysteresis*** on account of its analogy to the phenomenon associated with the demagnetisation of iron. The nature and area of these ***hysteresis*** loops (Schwartz and others) afford valuable data regarding the quality of a rubber.

TECHNICAL EXAMINATION OF RUBBER GOODS.

Crude rubber and vulcanised goods are frequently (on the part of the seller mainly with a view to control and improvement of manufacture, on the part of the buyer from the standpoint of ascertaining value or quality or of controlling contracts) submitted to chemical, physical, and mechanical tests.

Crude rubber. Substantially, the value of a crude rubber depends (*a*) on the quantity of actual rubber contained; (*b*) on the quality of the latter; (*c*) on the nature of such of the substances other than rubber which are non-removable by the ordinary works methods of purification (steeping and washing). The quantity of rubber is generally estimated by difference, determinations of moisture, resin, ash, nitrogen, and of insoluble matter giving the necessary data. There is a certain amount of overlapping between the 'ash,' 'nitrogen' (generally calculated as proteid), and 'insoluble' matter, which must be taken into consideration. The estimations referred to are, if possible, carried out on *washed* goods, and, naturally, when working in this way, 'washing loss' must be allowed for. With regard to the quality of the rubber, some basis of comparison between different samples of the *same species* is afforded by a determination of the viscosity of their solutions, but the best method undoubtedly is that of vulcanisation. In ordinary vulcanising experiments the aim should be to obtain the *best* cure, and, as this varies considerably for different rubbers, it is apparent that it is difficult to enunciate any simple standard vulcanisation test. Vulcanised samples should be tested certainly in regard to their mechanical properties, and, also, where possible, in regard to behaviour on storage. In special cases, of course, chemical and physical tests (*cf.* below) will be useful.

Vulcanised goods. Chemical analysis and physical and mechanical tests are employed by the manufacturer with a view to matching samples and for controlling, improving, and investigating defects in manufacture. The buyer, as a rule, tests the goods in order to ascertain whether they conform to a sample, contract or specification.

Chemical analysis is employed with a view to determine *inter alia* (*a*) the state of vulcanisation (*sulphur combined with rubber and free sulphur*); (*b*) substances soluble in acetone (rubber resins, oils, paraffin, &c.); (*c*) substances such as *bitumen, pitch, and tar*; (*d*) saponifiable matter (*'substitutes' made from vegetable oils, &c.*); (*e*) other 'fillers' (chiefly *mineral matter*, occasionally *fibres, free carbon, starch*); and (*f*) rubber, the presence of old (scrap) rubber or 'reclaimed.' 'Rubber' is generally determined by difference, the presence of 'reclaimed' or waste rubber may generally be inferred with considerable certainty if the 'combined' sulphur is high, the acetone extract abnormal, and the tensile tests show poor results.

Physical and physico-chemical tests which have practical value include (*a*) the determination of the effects of various reagents such as acids, alkalis, oils, &c., on the weight, volume, and mechanical properties of the material; (*b*) steam and dry heat tests; (*c*) electrical tests such as specific resistivity, surface resistance, and dielectric strength; (*d*) specific gravity, porosity, permeability, bursting tests, &c.

Mechanical tests comprise *inter alia* general tensile tests (*breaking strain, elongation at break, nature of curves at intermediate loads, elongation at constant load* and vice versa, *repeated stretchings, hysteresis tests*, &c.), compression tests (*compressions corresponding to specific loads, repeated compression, hammer test, recovery after compression for specific time*, &c.), abrasion tests, hardness tests, and elasticity tests.

The following is a list of a few of the more important works dealing with subjects referred to in the above article.

Bibliography. (*a*) *General.* Rubber (P. Schidrowitz, Methuen, 1911). India-Rubber and its Manufacture (H. L. Terry, Constable, 1907). Rubber, Gutta-Percha, and Balata (F. Clouth).

(*b*) *Cultural* and *botanical.* The Physiology and Diseases of Hevea Brasiliensis (T. Petch, Dulau, 1911). Hevea Brasiliensis or Para Rubber (H. Wright, Maclaren, 1912).

(*c*) *Manufacture.* Crude Rubber and Compounding Ingredients (H. C. Pearson, India-Rubber Publishing Co., 1910). The Manufacture of Rubber Goods (Heil & Esch; English ed., Griffin, 1909).

(*d*) *Chemistry, analysis,* and *testing.* Der Kautschuk u. Seine Prüfung (Hinrichsen & Memmler, Hirzel, 1910). Die Analyse des Kautschuks, &c. (Ditmar, Hartleben, 1909). The Chemistry of India-Rubber (C. O. Weber, Griffin, 1902). P. S.

RUBERYTHRIC ACID, or **Ruberythrinic acid** *v.* ALIZARIN AND ALLIED COLOURING MATTERS; also GLUCOSIDES.

RUBIA KHASIANA. According to Watt (Dictionary of the Economic Products of India, vol. vi. 571), there exists a variety of the *R. cordifolia* (Linn.) to which he has assigned the name of *R. khasiana.* This form, according also to Watt, is the richest in madder dye principle. It is occasionally met with in Sikkim, but attains its greatest development eastward in the Khásia and Naga Hills. It seems nowhere to be met with to the west of Sikkim. This dyestuff, according to Perkin and Hummel, yields colours precisely similar to those given by *R. cordifolia* and *R. sikkimensis* (Kurz), but it possesses a somewhat greater colouring power than either (J. Soc. Chem. Ind. 1894, 13, 348).

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RUBIA SIKKIMENSIS (Kurz). This Indian dye-stuff is closely allied botanically to *Rubia cordifolia* (Linn.); the dried root, which has a rough fluted appearance, is covered with a thick powdery layer of a grey pith-like substance, and looks altogether different from the round, smooth, straight roots of *R. cordifolia.* It occurs along with the allied species above mentioned in Sikkim and eastward to the Khásia and Naga hills where it is perhaps the most common as it is certainly the largest and most handsome species. Although the root has long been collected and sold in the bazaars at Darjeeling, the plant was not named or even known to exist prior to 1874, having escaped the attention of botanists, who appear to have mistaken it for *R. cordifolia.* The Lepchas of Sikkim do not appear to know that *R. sikkimensis* yields the madder dye, but in the Naga hills and in Manipur this species alone supplies the brilliant red dye used by the hill tribes (see Dyes and Tans of India, 154; Special Catalogue of Exhibits by the Government of India, Colonial and Indian Exhibition, 1886).

The examination of this root, by an identical process to that detailed in connection with Munjeet (*R. cordifolia*), has indicated that the phenolic constituents are *purpurin, mungistin* and *purpuroxanthin.* A trace of a red colouring matter approximating to $C_{15}H_8O_6$ in formula was also isolated, but the individuality of this compound has not been definitely established.

Dyeing properties. The application of *R. sikkimensis* root in dyeing presents no difficulty.

Calico printed with iron and alumina mordants may be dyed without any addition of calcium carbonate or acetate to the bath since there is a sufficiency naturally present in the root. Generally speaking, the colours with the different mordants are similar to those obtained from madder, but the reds and chocolates are much bluer being devoid of yellow, and the lilacs are decidedly greyer. The colours, however, are precisely similar to those obtained from *R. cordifolia*, the latter possessing nearly a half more dyeing power.

Comparing the colours on ordinary stripe mordanted calico given by pure purpurin and *R. sikkimensis*, a very marked difference is noticeable; the former gives very yellowish-reds and chocolates, full pinks and purplish lilacs, while the latter yields very bluish-reds and chocolates, bare pinks and greyish lilacs.

The dyeing power of *R. sikkimensis* is equivalent to its containing 0·37–0·5 p.c. purpurin

(Perkin and Hummel, Chem. Soc. Trans. 1883, 63, 1157). A. G. P.

RUBIACIC ACID, RUBIACIN, RUBIADIN. *Rubianin v.* MADDER.

RUBIADIN GLUCOSIDE *v.* GLUCOSIDES.

RUBIADIPIN, RUBIAFIN *v.* MADDER.

RUBIANIC ACID *v.* GLUCOSIDES; ALIZARIN AND ALLIED COLOURING MATTERS.

RUBIDEHYDRAN *v.* MADDER.

RUBIDINE *v.* AZO- COLOURING MATTERS.

RUBIDIUM. Rb. At.wt. 84·78 was discovered by Bunsen and Kirchoff by means of the spectroscope in 1861. In small quantities, rubidium is very widely distributed in nature; it occurs in many minerals such as *leucite, triphylite, porphyrite, mica, orthoclase, carnallite* (Feit and Kubierschky, Chem. Zeit. 1892, 16, 335); in nearly all iron ores, in some aluminous minerals and in many meteorites (Hartley and Ramage, Chem. Soc. Trans. 1897, 533, 547). It is also present in many mineral springs, in sea water, seaweed, beetroot, tobacco, in various kinds of coffee and tea, in crude cream of tartar, in potashes from various sources and in the ash of the oak and of some beech trees, but rubidium cannot replace potassium as a plant food. For modes of separation from its minerals and from caesium, *v.* Muthmann (Ber. 1894, 26, 1019, 1425); Formánek (Oesterr, Chem. Zeit. 1899, 2, 309); Feit and Kubierschky (*l.c.*); Lemoine (Bull. Assoc. Belge des Chim. [9] 12, 344); Wells (Amer. Chem. J. 1901, 26, 265); Archibald (Chem. Soc. Trans. 1904, 776). The metal can be obtained by heating a mixture of sugar charcoal, ignited acid rubidium tartrate and calcium carbonate at a white heat, or by distilling the hydroxide with magnesium (Erdmann and Köthner, Annalen, 1896, 294, 55).

Hackspill prepared metallic rubidium by heating the chloride with metallic calcium in an iron boat in a vacuum and then distilling off the metal (Compt. rend. 1905, 141, 106).

Rubidium is a silver white readily volatile metal of sp.gr. 1·52, m.p. 38·5° and b.p. 696°. Like potassium, it forms amalgams with mercury, an explosive compound with carbon monoxide, oxidises rapidly in air and burns in water with liberation of hydrogen. Many of the minerals in which it occurs and its salts are radioactive (Campbell, Proc. Cambs. Philos. Soc. 1909, 15, 11; Strong, Amer. Chem. J. 1909, 42, 147; Büchner, Proc. K. Akad. Wetensch, Amsterdam, 1909, 12, 154).

The salts of rubidium are isomorphous with, and very similar to, the corresponding potassium, ammonium, and caesium salts.

The *oxide* Rb_2O (Rengade, Compt. rend. 1906, 143, 1152), also the *oxides*, Rb_2O_2, Rb_2O_4, Rb_2O_3 (Rengade, *ibid.* 1906, 142, 1533; 1907, 144, 920), and the hydroxide Rb(OH), a greyish-white deliquescent mass (Forcrand, Compt. rend. 1906, 142, 1252) have been prepared.

Rubidium peroxide hydrate $RbO{\cdot}OH,H_2O_2$, forms snow white deliquescent crystals, stable below 0°, but decomposes violently at the ordinary temperature with evolution of oxygen and deposition of a hydrated form of the oxide Rb_2O_4 (Peltner, Ber. 1909, 42, 1777).

Rubidium hydride RbH, is formed when the metal is heated in a current of hydrogen at 300°. It forms colourless prismatic needles and is readily attacked by the halogens, oxygen and sulphur. With phosphorus it yields phosphine; with nitrogen, a mixture of the nitride and amide is formed. When heated with carbon dioxide it yields the formate, and with sulphur dioxide, it forms a mixture of sulphide and sulphate at ordinary pressure, and a hyposulphite, $Rb_2S_2O_4$ at diminished pressure. With ammonia, the hydride reacts thus

$$RbH+NH_3=RbNH_2+H_2$$

(Moissan, Compt. rend. 1903, 136, 587).

Rubidium chloride RbCl, forming glittering cubes and the corresponding bromides and iodides readily unite with the halides of a large number of metals forming crystalline double salts; similar double salts are also formed by many other rubidium compounds (Bilz and Herms. Ber. 1907, 40, 974; Weinland and Dinkelacker, Zeitch, anorg. Chem. 1908, 60, 173; Gutbier and Riess, Ber. 1909, 42, 3905. Rubidium also forms compounds containing a larger number of halogen atoms, such as $RbBr_3$, $RbClBr_2$, $RbCl_4I$, &c. (Herty and Black, Amer. Chem. J. 1896, 18, 847; Zeitsch. physikal. Chem. 1899, 28, 523; Abegg, Zeitsch. anorg. Chem. 1906, 50, 403; Foote and Chalker, Amer. Chem. J. 1908, 39, 561).

Rubidium ammonium bromide $RbBr+3NH_4Br$ is a white or yellowish crystalline powder which is recommended as a substitute for potassium bromide as an anti-epileptic and as a hypnotic (Laufenauer, J. Soc. Chem. Ind. 1890, 650, 888; Coblentz, *ibid.* 1898, 736).

Rubidium hydrogen fluoride RbF,HF is partially converted into rubidium fluoride, RbF, when heated with excess of ammonium hydrogen fluoride (Chabrie and Bouchonnet, Compt. rend. 1905, 140, 90; Eggeling and Meyer, Zeitsch. anorg. Chem. 1905, 46, 174).

Rubidium chlorate and *perchlorate, rubidium iodate* $RbIO_3$ (Wheeler, Amer. J. Sci. 1902, [iii.] 44, 123; Barker, Chem. Soc. Trans. 1908, 15), and the *periodate* $RbIO_4$ (Barker, *l.c.*) also exist. The *sulphate* (Silliman, Amer. J. Sci. 12, 30), *nitrate* (Jones, Chem. Soc. Trans. 1908, 1742), *trithionate* $Rb_2S_3O_6$ (Mackenzie and Marshall, *ibid.* 1735; Meyer and Eggeling, Ber. 1907, 40, 1351); *chromate* and *dichromates* (Schreinemakers and Filippo, Chem. Zentr. 1906, i. 1321; Wyrouboff, Bull. Soc. chim. 1908, [iv.] 3, 7; Stortenbeker, *ibid.* 481), *carbonates* and *percarbonates* (Peltner, *l.c.*; Forcrand, Compt. rend. 1909, 149, 97, 719), some *molybdates* (Herschfinkel, Zeitsch. anorg. Chem. 1909, 64, 263), *arsenates* (Bouchonnet, Compt. rend. 1907, 144, 641), *tungstates* (Schaefer, Zeitsch. anorg. Chem. 1904, 38, 142), various *phosphates* (Berg. Ber. 1901, 34, 4181), *tellurates* and *selenates* (Norris and Kingman, Amer. Chem. J. 1901, 26, 318) have been prepared.

Rubidium pentasulphide Rb_2S_5 is formed by warming the monosulphides with powdered sulphur and aqueous alkali hydroxide in an atmosphere of hydrogen. It crystallises in dark-red rhombic prisms, m.p. 223°–224° (Biltz and Wilke-Dörfurt, Ber. 1905, 38, 123). Other sulphides and hydrosulphides possibly, also exist (Zeitsch. anorg. Chem. 1906, 48, 297; *ibid.* 50, 67).

Rubidium ammonia $Rb.NH_3$ is prepared by the direct action of liquid ammonia on the metal at about −70° or of the gas at −3°; its solution in liquid ammonia is used for the preparation of the carbide (Moissan, Compt. rend. 1903, 136, 1177).

Rubidium acetylide acetylene $C_2Rb_2C_2H_2$ forms transparent hygroscopic crystals, m.p. 300°, which decompose with the formation of *rubidium carbide* C_2Rb_2 and acetylene (Moissan, Compt. rend. 1903, 136, 1217, 1522).

Rubidium syngenite $CaRb_2(SO_4)_2H_2O$, is obtained when finely divided gypsum is left in contact with a 30 p.c. solution of rubidium sulphate (D'Ans and Zeh, Ber. 1907, 40, 4912).

Rubidium forms *alums* with indium, vanadium, titanium and iridium.

Iron rubidium selenium alum

$$Rb_2Fe_2(SeO_4)_4,24H_2O$$

separates as pale violet crystals when rubidium carbonate is added to a solution of ferric hydroxide in excess of selenic acid. It has a sp.gr. 2·1308 at 15° and melts in its water of crystallisation at 40°–50°, forming a red liquid (Roncagliolo, Gazz. chim. ital. 1905, [ii.] 35, 553).

Z. K.

RUBIHYDRAN *v.* Madder.

RUBIRETIN *v.* Madder.

RUBRESCIN. A substance prepared by melting resorcinol with chloral hydrate. Dissolves in water giving a red solution, which is exceedingly sensitive to alkalis. Used as an indicator.

RUBRESSERINE *v.* Ordeal bean.

RUBRIC LAKE. *Madder lake v.* Pigments.

RUBY *v.* Corundum; also Aluminium.

RUBY-COPPER-ORE *v.* Cuprite.

RUBY-SILVER-ORE *v.* Proustite and Pyrargyrite.

RUBY SULPHUR. *Realgar, Arsenic sulphide, v.* Arsenic.

RUDDLE *v.* Reddle.

RUE, OIL OF, *v.* Oils, essential.

RUFIGALLIC ACID or **RUFIGALLOL** *v.* Alizarin and Allied colouring matters.

RUFIOPIN *v.* Alizarin and allied colouring matters.

RUM is an ardent spirit, the product of distillation of saccharine matter derived from the sugar cane. It is usually made from molasses, or from the skimmings of the sugar boilers and the waste of the crushing-house, or (when the cost of production of sugar makes it profitable) from the sugar cane. The principal source of supply is the West India Islands and British Guiana, and the quality most esteemed is associated with the name of Jamaica. It is also distilled in France from beetroot.

The term 'rum' is by some thought to be derived from the final syllable of 'saccharum.' It is certain, however, that so long ago as 1650 this spirit was known in the West Indies as 'rumbullion,' an old Devonshire term for an uproar, disturbance, or tumult, the word being subsequently contracted into 'rum.' An old writer of that period, speaking of Jamaica, states, 'The chief fudling they make in this island is "rumbullion," alias "kill-devil," and this is made of suggar canes distilled, a hott, hellish, and terrible liquor.' It is well-known that many Devonshire colonists settled in the West Indies, and the term 'rumbowline' is said still to linger amongst certain seafaring men in referring to grog. The earliest official mention of this spirit under the name of 'rum' appears to be in an order of the Governor and Council of Jamaica dated July 3, 1661.

The rums of Jamaica and Demerara (British Guiana) represent the two principal types of rum in commerce, the different characters of these being due not only to the nature of the soil and therefore of the products from the sugar-cane, but also to differences in the methods of fermentation, distillation, and mode of manufacture generally.

In the first type the wash is set at a relatively high density (from 1072 to 1096), and the fermentation is slow, lasting from a week to a fortnight, or even longer, whilst in the second the wash is set at a low density (about 1060), and the fermentation lasts only from 30 to 48 hours. In Jamaica, moreover, pot-stills only are used, whilst in other West India Islands, in Trinidad, and British Guiana patent stills are commonly employed, the former resulting in a comparatively low, and the latter a relatively high. production of alcohol.

The following account of the manufacture of Jamaica rum was given before the Royal Commission on whisky and other potable spirits by Mr. Nolan, Special Commissioner of the Jamaica Government to the United Kingdom: 'Jamaica rum is made from sugar-cane in the old pot-still. The sugar-canes, when ripe, are cut and carted into the works (the canes ripen in from 12 to 15 months). They are passed through a strong steel or iron three or five roll mill worked by steam. The juice of cane liquor falls through the rolls on to a receptacle directly under the mill, which is called the mill-bed. The liquor is carried from the mill-bed by gravitation to another receptacle, which is called the well. From this well it is pumped to large iron vessels called siphons or clarifiers which contain from six to seven hundred gallons. In the bottom of the siphons there are copper steam coils or tubes, which are filled with steam when the siphon is full. The liquor is thus heated to a few degrees below boiling-point. By this means all the scum comes to the top, and the rest of the liquor in the siphon is partially clarified. The clarified liquor is then gradually drawn off by a cock at the side of the siphon low down, until the scum alone is left. The clarified liquor is either sent to the boiling-house to make sugar or passed through other vessels to clarify to a higher degree, as really the whole process of sugar-boiling is to eliminate foreign matters (which take the form of scum) from the liquor, and then remove the water by evaporation. The scum or dirty liquor which remains in the siphon is then drawn off and sent to the still-house, where it is allowed to remain for a few days till it sours. The siphons are also washed out with water, and such water is sent to the same receptacle in the still-house. In fact, all the washings and scums from vessels in the boiling-house are sent to this receptacle. There is also put into this receptacle at the beginning of crop a certain amount of megass (the fibrous part of the cane which remains after crushing the juice from the cane in the mill), which assists to sour the liquor. In the meantime the clarified liquor in the boiling-house is made into sugar and allowed to cool. It is then passed through centrifugals, or purgers, which separate the molasses from the dry sugar on somewhat the same principle as a milk separator. The molasses are then rich, and at this point are sent to the still-house. The only other ingredient used in the manufacture of Jamaica rum is *dunder*. This is a substance which remains at the bottom of the pot-still after all the spirits and a great quantity of the water have been evaporated by distillation from the wash. It is removed from the still and allowed to cool for a few days. It comes from the still with something like the consistency and colour of pea-soup. There are three ingredients, with water used in the setting up of the wash for fermentation, all of which are the products of sugar-cane, viz. scum or skimmings, molasses and dunder. They are used in proportions according to the judgment and practical experience of the distiller, who is guided by all circumstances connected with the estate and distillery. The fermentation is from six to twelve days, in some cases longer. After the fermentation subsides, the wash is pumped into a pot-still. Jamaica has at all times used the pot-still; and there is no other used in the island.'

Until comparatively recently the fermentation process was left very much to chance, but, commencing in 1903, special investigations have been, and are still being, made in Jamaica into the chemistry and bacteriology of the manufacture of rum, with special reference to the micro-organisms concerned in the fermentation processes, and their influence on the character, quality, and flavour of the rum. It was found that the peculiar and characteristic flavour of Jamaica rum was largely due to acidic and putrefactive fermentation by bacteria.

According to Cousins (West India Bulletin, vol. 8, No. 1, 1907), there are three classes of Jamaica rum, viz. (1) 'local trade quality,' for home consumption; (2) 'home-trade quality,' for consumption in the United Kingdom; and (3) 'export trade quality,' for exportation to the Continent of Europe.

The rums of the first class have usually a lower ether content (sometimes as low as 90 parts per 100,000) than the second, and an inferior flavour. They are the result of light settings and quick fermentation. The stills are heated by steam coils and double retorts are used. These rums constitute the 'wine of the country,' and are consumed almost exclusively by the lower orders in the island.

The second class, sometimes described as 'public-house rums,' are those exported to and usually known in the United Kingdom as 'Jamaica rum.' This constitutes the bulk of the rum exported from Jamaica.

The flavour of these is characterised by a heavy residual 'body,' due mainly to esters of acids of high molecular weight. These acids are not producible from sugars, and are almost absent in rums other than Jamaican, produced from diluted molasses without dunder or acid skimming and distilled in patent stills. Investigations made in the Government Agricultural Department in Jamaica indicated that the higher acids result from the bacterial decomposition of the dead yeasts found in the distilling materials.

The best types of these 'home-trade' rums contain from 300 to 500 parts of esters, and the bulk of the rums of this class about 200 parts per 100,000, but in some cases the ether content even of genuine home-trade rums of good quality falls as low as 100.

These rums are generally produced by a slower type of fermentation than the 'local trade' rums, the fermentation period sometimes extending over a fortnight, although even this is not so prolonged as the fermentation period of the export rums described below.

As compared with the 'local trade' rums, they have a fuller and more fruity aroma, and on dilution the spicy residual flavour is more strongly marked. The latter is due to the larger proportion of higher alcohols present, and these, in excess, are apt to cause an objectionable cloudiness on dilution. The remedy for this is to test the spirit with water before accepting it as rum, retaining a cloudy distillate for further distillation, and the fermenting vats should be limed to secure a clearer fermentation. Another defect sometimes observed in these rums is a burnt flavour (best detected on dilution with water) due to the use of a 'direct fire' still, and the remedy in this case is to heat the stills with a copper coil. A 'fruity' aroma is sometimes obtained by the addition of pineapples or guavas to the wash in the still.

The rums of the third class, or 'export trade,' quality differ much more widely from the 'local' and 'home trade' rums than these do from each other. Rums of this type are characterised by an abnormally high proportion of esters, and are exported mainly to the Continent of Europe, principally to Germany. They are not suitable for direct use as a beverage, but are blended together and vatted off with lighter rums or even with neutral spirit to impart to the latter a rum character. They are also used to fortify and give body to hock and similar wines.

These 'export' rums, or 'German-flavoured,' as they are commonly called in Jamaica, are produced on the north side of the island on comparatively small estates where, owing to certain disadvantages under which they labour as sugar-producing estates, it is more profitable to manufacture rum than sugar.

Instead of 30 hours' fermentation, which suffices for certain rums of the Demerara or Trinidad type (*v. infra*), these 'German-flavoured' rums require a fermentation period lasting from a fortnight to three weeks, and the process is conducted in a strongly acid wash. The organisms are of the fission type, and are able to attenuate a liquor with an acidity of 3 p.c., whilst the ordinary oval budding yeast is paralysed by an acidity of less than one-fifth of this amount.

The proportion of esters in these rums is relatively very high, varying from 500 to 1200, and in some instances reaching 1500 or more parts per 100,000. According to Cousins, about 97 p.c. of these esters consist of acetic ester and 2 p.c. of butyric ester; traces of formic ester may be present, and from ½ to ¾ p.c. of the total consists of heavy esters derived from acids of high molecular weight. It is upon the latter that the character and to a large extent the commercial value of the rum is said to depend.

" tiddy, rum dum, dum

The acetic and butyric esters may be considered merely as media for the conveyance of the aroma of the heavier esters, which are best recognised by smell after diluting with water, thereby reducing the vapour tension and pungency of the more volatile esters. The latter are best appreciated before diluting the spirit.

A process for reinforcing the content of the natural esters of rum by recovering the volatile acids left in the spent liquor from the retorts and using them in a subsequent operation has been carried out on a commercial scale by Cousins. The acids in the lees are fixed with lime, the residue evaporated to dryness, and the acids liberated by the requisite amount of sulphuric acid, recovered by distillation, and returned into the process. By this means rums containing as much as 3500 parts of esters per 100,000 have been obtained. The process appears to be equally applicable to brandy and whiskey.

Pot-still rum when new has a rather disagreeable odour, but the true characteristic flavour develops by storing in wooden casks, and continues to improve for eight or ten years. Rum matures more rapidly, however, than either brandy or whiskey.

The rum of British Guiana, usually known as 'Demerara' rum, is made almost exclusively from vacuum pan molasses with the occasional addition of other sugar-containing waste products of the sugar factories.

The following account of Demerara rum, as made in British Guiana, is taken from a statement drawn up by the British Guiana Planters' Association and transmitted to the Royal Commission on Whiskey and other Potable Spirits, 1909 :—

'In British Guiana the wash (wort) is prepared by diluting molasses with water to a density of 1060, and rendered slightly acid by the addition of sulphuric acid in quantity sufficient to set free more or less of the combined organic acids, but so as not to have uncombined sulphuric acid present in the wash; whilst n some of the distilleries additions of sulphate of ammonia in small proportions are made to the wash, in order to supply readily available nitrogenous food for the yeasts and thus to enable them to multiply with rapidity and to retain a healthy active condition. The reason or rendering the wash slightly acid is to guard against the excessive propagation of the butyric and lactic organisms and to render it more uitable for active alcoholic fermentation. Within a very short time from the molasses being diluted it enters into vigorous fermentaion, and the fermentation rapidly proceeds to omplete attenuation.

'In British Guiana the distilleries are of hree kinds: (1) those using pot-stills or vattills, which are practically only modified pottills; (2) those using both pot-stills or vat-stills nd Coffey or other continuous rectifying stills; nd (3) those using only Coffey or other coninuous rectifying stills. Out of forty-two istilleries in operation, thirty-two use pot- or at-stills only; three have both pot- or vat-stills nd continuous stills, whilst seven possess continuous stills only.

'Vat-stills consist of cylindrical wooden essels built of staves strongly hooped with wrought-iron. They have high copper domes covering openings in the heads of the vessels which communicate with a retort or retorts of the Jamaican pattern, but as a rule the retort acts as the lowest vessel of a rectifying column. As in Winter's still, a spiral pipe or a series of small perpendicular pipes descend down the interior of a column through which cold water is run whenever distillation is in progress, and by which the spirit vapour undergoes a process of rectification as it ascends the column before passing into the condenser. The vat-stills are heated by injection of steam. The Coffey or continuous rectifying stills are of the usual well-known types.'

By means of the patent stills some of the estate distilleries in British Guiana are able to produce approximately one proof gallon of spirit for each five degrees of attenuation from every hundred gallons of wash, or about 90 p.c. of the theoretical yield. The greater part of the patent still spirit is consumed locally, and this local preference for the lighter types of rum obtains in other West Indian colonies, and has already been noticed in connection with the 'local trade' rum of Jamaica.

Compared with Jamaica rums, the proportion of esters in rums of the Demerara type is very low, but varies considerably. The results of determinations, made in the Government Laboratory of British Guiana, of the esters (calculated as ethyl acetate) in over 400 samples of rum examined during the years 1901–1908, showed a minimum of 63 and a maximum of 104 with an average of 81 parts per 100,000 of absolute alcohol by volume.

According to Girard and Cuniasse (Analyse des Alcools et des spiritueux), the average proportion of esters and other secondary products comprised in the 'co-efficient non-alcohol' (*v.* Brandy) found in ordinary rums of commerce known to be genuine, are shown in the following table expressed in relation to 100,000 parts per volume of absolute alcohol :—

	Min.	*Max.*	*Average.*
Acidity (as acetic acid) .	158·4	400·0	250·8
Aldehydes (as acetic aldehyde)	0·3	54·5	24·4
Furfural	1·2	50·0	7·1
Esters (as acetic ester) .	105·7	443·1	229·5
Higher alcohols (*iso*butyl standard) . . .	52·0	308·6	140·4
Coefficient of secondary products	432·7	919·0	652·5

Details of methods for determining the secondary products may be found in the Minutes of Evidence taken by the Royal Commission on Whiskey and other Potable Spirits, 1909 (vol. 2, Appendix Q, xii.).

The colouring matter usually employed consists of caramel made from burnt molasses or sugar, but care should be exercised in its use so as to avoid excessive 'obscuration' or apparent diminution of strength as shown by the hydrometer or alcoholometer. The 'obscuration' should not exceed 1½ p.c. of proof spirit, and the tint of a fully coloured rum should correspond with about No. 19 on Lovibond's tintometer.

The strength of rum as imported into the United Kingdom varies from about 20 underproof to 50 or more overproof, the average being 35 overproof, equivalent to 77 p.c. of absolute alcohol by volume. The lowest limit of strength for the sale of rum under the Food and Drugs Acts is 25 underproof unless the fact of its dilution to a lower strength is declared.

The British Customs distinguish between rums from Jamaica, rums from other sugar-cane producing countries, and 'imitation' rums, a term applied to spirits of rum character, imported from countries in which the sugar cane is not cultivated.

The quantity of the latter imported is insignificant compared with genuine rum, and during the last decade it has declined from about 44,000 proof gallons in 1900 to not more than 6000 proof gallons in 1910, whilst the quantities of genuine rum imported during the same periods were over 4,000,000 proof gallons in 1900 and nearly 3,000,000 proof gallons in 1910. Of this, about two-thirds came from British Guiana ('Demerara' rum) and about one-quarter from Jamaica.

The proportion of rum consumed per head in the United Kingdom has gradually declined (in common with other spirituous liquors, including beer and wine) during the last decade, being in the case of rum equivalent to 0·11 gallon per head of the population in 1900 as compared with 0·05 gallon, or less than half the quantity, per head in 1910.

'*Imitation rum*' is made either by the addition of heavily flavoured rums rich in esters or artificial 'essence of rum' (*v. infra*) to plain spirit from potatoes or beet molasses, with addition of colouring matter.

As an example of an artificial rum 'essence,' the following is given by Fleischman (The Art of Blending and Compounding Liquors and Wines). A mixture consisting of 32 ozs. of alcohol, 4 ozs. of sulphuric acid, 2 ozs. of manganese dioxide, and 4 ozs. of pyroligneous acid is distilled, and to 32 ozs. of the distillate are added 32 ozs. of acetic ester, 8 ozs. of butyric ester, 16 ozs. of saffron extract, and ½ oz. of oil of birch. For a low grade artificial rum Fleischman gives the following recipe: plain spirits, 40 gallons; rum, 5 gallons; prune juice, ½ gallon; caramel, 12 ozs.; and 'rum essence' (prepared as above), 8 ozs.

Rum shrub is rum-flavoured with orange and lemon and sweetened with sugar. It may be made on a small scale from the following recipe: To 1 gallon of rum add 1 pint each of orange and lemon juice and the peels of two oranges and 1 lemon. Digest for 24 hours in the cold, strain, and sweeten with a syrup made by dissolving 4 lbs. of white sugar in 5 pints of water.

West India shrub is very similar to the above, the orange and lemon juice being replaced by an equal quantity of lime juice. J. C.

RUSSET RUBIATE. *Rubens madder v.* PIGMENTS.

RUST. The red or reddish-brown incrustation formed on iron and steel when exposed to ordinary atmospheric influences. Iron is singular in that the film first formed, instead of protecting the metal beneath from further action, as in the case of other oxidisable metals such as zinc and aluminium, continues to increase in thickness until a rough earthy crust is formed, which is easily detached in flakes. The process may continue until the iron is wholly converted into rust.

The change is finally one of oxidation, as rust consists mainly of partially-hydrated ferric oxide, its composition lying between Fe_2O_3 and $Fe_2(OH)_6$. But rust may contain notable quantities of ferrous oxide in the layers next the metal, and Tilden (Chem. Soc. Trans. 1908, 1362) quotes the analysis of a specimen of rust about 250 years old, with about one-seventh of the iron still in the ferrous state. Graphitic and other impurities insusceptible to oxidation will also accumulate in the rust of iron.

The exact conditions which induce and maintain the process of rusting have been the subject of much elaborate investigation. The problem presents itself in two distinct aspects. There is the question, primarily of scientific interest, as to the chemical mechanism of the process; on the other hand, there is the study of rusting as it occurs under industrial conditions.

Experiments with iron prepared by the electrolysis of its highly purified compounds; with water freed as far as possible from dissolved material; with an atmosphere under strict control; obviously do not represent ordinary working conditions, where iron is both physically and chemically a composite material and both water and air are contaminated with accessory constituents. Whilst there is great difficulty in solving the more theoretical question, it is a much simpler matter to investigate the conditions under which the rusting of iron in ordinary circumstances is stimulated or retarded, although the number of variables in the problem limits the possibility of drawing general conclusions.

Theories of rusting. All observers agree that liquid water and a supply of oxygen are essential to the rusting process. The difference of opinion is chiefly as to whether these alone are sufficient to induce and maintain the process. It is impossible here to review or discuss the voluminous literature which has appeared on the subject during recent years, and for particulars, including bibliography, the reader is referred to Friend's Corrosion of Iron and Steel (Longmans and Co., 1911), and to The Corrosion and Preservation of Iron and Steel, by Cushman and Gardner (McGraw-Hill Book Co., New York, 1910). It will suffice here to give a short account of the questions at issue.

The assumption that iron will rust in presence of air and water alone, appears to have been general until 1871, when Crace Calvert (Chem. News, 23, 98), from differential experiments with air, water, and carbon dioxide, concluded that their conjoint action was necessary. Crum Brown (J. Iron and Steel Inst. 1888, II. 129) supported this theory and gave precision to it. The iron, it is supposed, is first attacked by dissolved carbon dioxide (carbonic acid) giving ferrous carbonate, or bicarbonate, and hydrogen. The ferrous salt is then oxidised by atmospheric oxygen, and the basic ferric carbonate potentially formed is, in presence of water, converted into hydrated ferric oxide (rust). As the carbon dioxide is thus wholly eliminated at the end of the cycle, it may be supposed to renew its attack on the iron.

This theory of rusting was generally accepted until 1903, when Whitney (J. Amer. Chem. Soc. 25, 394) applying modern electrochemical theory to the process, expounded the view that water and air alone suffice to establish rusting. According to modern views, the action of an acid on a metal is ascribed to an exchange of electric charges between the hydrogen ions of the acid and the electrically neutral atoms of the metal, the hydrogen being deposited on the metal in the molecular state, and the metal atoms passing into the solution as metal ions. The process is analogous to the deposition of metallic copper on iron from a solution of copper sulphate. The discharge of each copper ion and its deposition as copper brings a ferrous ion into the solution. Inasmuch as pure water is regarded as being to some small extent ionised into hydrogen ions and hydroxyl ions, it is to that extent, electrochemically speaking, an acid, and when iron is immersed in it, there should be a deposition of hydrogen on the iron and an equivalent formation of iron ions. The water round the iron now contains ferrous ions and hydroxyl ions, or in common language, is a dilute solution of ferrous hydroxide. If oxygen has access to the ferrous hydroxide solution, hydrated ferric oxide will be formed and deposited as rust.

Such in outline is Whitney's theory, apart from the detailed application of Nernst's theory of electrolytic solution pressure, which he also introduces. The explanation just given for the action of pure water on pure and physically homogeneous iron, involves the deposition of hydrogen as a film of gas on the immersed portion of the metal. As this film would prevent further contact between the metal and the water, it is supposed that it slowly dissolves in the water and escapes by diffusion, or is oxidised by the dissolved oxygen, so enabling the action to continue.

Another theory of rusting was advanced by W. R. Dunstan, according to which air and water alone were sufficient to cause rusting with the transitory production of hydrogen peroxide (*cf.* Dunstan, Jowett, and Goulding, Chem. Soc. Trans. 87, 1548). Although this theory is in accord with a number of facts and has been fruitful in stimulating research, it is unnecessary to give further details, as in a later paper (Dunstan and Hill, *ibid.* 1911, 99, 1835), the authors no longer hold that it is adequate to explain all the observed phenomena. They still maintain, however, that water and oxygen alone are sufficient to initiate and maintain the rusting process.

The enunciation of the newer theories has led to much investigation, the chief object being to decide whether iron will rust in air and water when every precaution is taken to exclude carbon dioxide. Moody (Chem. Soc. Trans. 1906, 89, 720), as the result of careful experiments directed to this special point, concluded that water and oxygen alone were insufficient to induce rusting. In experiments where iron had remained bright for many weeks the introduction of a minute quantity of carbon dioxide at once determined rusting. The experiments of Friend (J. Iron and Steel Inst. 1908, II. 16) also led to the same conclusion. On the other hand, Cushman (The Corrosion of Iron, Bulletin No. 30, U.S. Dept. of Agric. 1907), Tilden (Chem. Soc. Trans. 1908, 93, 1358), Heyn and Bauer (Mitt. Königl Material-prüfungsamt, 1908, 26) conclude that water and oxygen alone suffice to cause and maintain rusting.

Nearly all the experiments just referred to were carried out with iron of ordinary commercial purity. This circumstance made it possible for supporters of the 'acid theory' to ascribe the rusting in absence of carbonic acid, to the presence of acidic substances generated from impurities in the iron itself. Lambert and Thomson (Chem. Soc. Trans. 1910, 97, 2426) found that carefully purified iron remained unchanged when exposed for several months to purified air and water. Any specimen of commercial iron, or of iron prepared with fewer precautions than the immune sample, rusted quite readily under the same circumstances. From their experiments, the authors concluded that whilst pure iron will not rust in pure air and pure water, iron will do so if it contains only a small amount of impurity, even if the impurity is neither acid in itself nor likely to give rise to acid.

The one positive and indisputable conclusion which seems deducible from the foregoing summary of experimental results is that contamination of the air or water with carbonic acid, and of the iron with 'impurities' in general, facilitates the rusting process. Apart from that, there is obviously direct contradiction. In the latest paper already referred to, Dunstan and Hill (*l.c.*) adduce evidence, which, if accepted, affords an explanation of many discrepancies. Their experiments go to show that in all cases where the rusting process failed to occur in the presence of air and water alone, the iron had been rendered 'passive' by its preliminary treatment, passivity being shown by the inability of the iron to dissolve in nitric acid of sp.gr. 1·2 or to precipitate copper from a dilute solution of copper sulphate. An exception must be made in the case of the highly purified iron of Lambert and Thomson, with regard to which it is held rather that the case conforms to 'the general experience that chemical change is invariably retarded when highly purified materials are employed.' Dunstan and Hill found that carbonic acid destroys the passivity of iron and in that way may indirectly initiate the rusting of such iron. The normal rusting process they regard as due to the direct action of the oxygen dissolved in water. Iron does not first pass into solution, but ferrous hydroxide is formed on the iron itself and is afterwards oxidised to the ferric state. With regard to the production of the passive state, Dunstan and Hill record a large number of observations relating to iron and other metals and favour the view that it is due to the presence of a film of oxide on the surface of each metal. In the case of iron, the film (Fe_3O_4) remains intact on heating in a vacuum to 400°; in hydrogen it is destroyed at 250°.

When we consider the rusting of iron as a practical question in the light of the foregoing experiments and theories, it may be said that whatever be the detailed atomic transactions of the process, the broad outlines of a working hypothesis are readily drawn. Commercial iron is never chemically nor physically homogeneous, water is never free from an electrolyte. Any electrochemical theory teaches that when iron and water of this kind come in contact, the conditions for electrolysis are present. The condition of things does not differ essentially from that where a rod of purified zinc and a platinum wire are immersed in dilute sulphuric acid. When the protruding ends of the metals are connected directly, or by a conductor, the zinc dissolves and hydrogen escapes from the platinum. If commercial zinc be used alone, local circuits are formed on its surface; in one place the metal dissolves, whilst in another hydrogen is disengaged at the surface of an adjacent impurity. If the zinc be amalgamated the metal becomes coated with a homogeneous film of zinc amalgam; local circuits are no longer possible, and so the action of the acid ceases.

These electrochemical facts are fully applicable to the case of iron, and would lead us, in considering the cause and prevention of rust, to look first to the physical and chemical heterogeneity of the metallic surface.

The ferroxyl indicator. The study of the susceptibility of iron to rust, and especially of the localisation of susceptibility, has been aided considerably by a device due to Cushman (*l.c.* and J. Iron and Steel Inst. 1909, I. 33) and Walker (J. Amer. Chem. Soc. 1907, 29, 1257). The iron to be studied is fixed in a jelly made of agar-agar, in which small quantities of phenolphthalein and potassium ferricyanide have been incorporated. Wherever the iron is being attacked, blue ferrous ferricyanide (Turnbull's blue) appears, whilst the second electrode in the circuit declares itself by the pink colour developed from the phenol-phthalein. The pink colour results from alkalinity, or in modern language, hydroxyl ions; but whether this is due merely to the electrolysis of the potassium ferricyanide and the liberation of potassium at the negative points of the iron surface, or whether it is also due to the direct electrolysis of water, need not be discussed.

Influence of physical and chemical heterogeneity on the rusting process. By use of the ferroxyl indicator, confirmation can be obtained of some generally accepted opinions in regard to the rusting of iron. In the first place it can be shown that a want of physical homogeneity in itself aggravates the process. Thus the laminations of a metal become clearly marked in the indicator; the cut ends of a rod where the metal has been subjected to strain are seen to differ electrochemically from the rest of the rod; indentations, scratches, or other injuries become centres of corrosion.

When we come to consider the influence of chemical heterogeneity the problem is much more difficult. It is not easy to say, for example, what is the relative corrosibility of cast-iron, wrought iron and the various kinds of steel. Dogmatic statements on the subject are often met with, justified no doubt by a certain range of experience: but there are so many varieties of the three 'metals' and so many different conditions under which they may be compared, that a single generalisation is hardly possible.

Cobb (J. Iron and Steel Inst. 1911, I. 170) finds (i) that pure iron is definitely electro-positive to most of its impurities—that is, a current is found to flow through the liquid from iron to impurity, the iron going into combination with some substance in the liquid, and the impurity remaining undissolved. Among such impurities were found phosphide, sulphide, carbide, oxide, and silicate of iron. With carbon (graphite), the effects were particularly marked. All the iron alloys tried (excepting ferro-manganese) were also electro-negative to pure iron. (ii) With the sulphide and silicate of manganese, little or no current flowed, because both were non-conducting. (iii) Manganese and 80 p.c. ferro-manganese were found definitely electro-positive to iron, manganese going into solution, while iron remained undissolved. (iv) Every piece of commercial iron showed electrical effects with any other, and the effects between portions of the same piece were always sufficient to induce corrosion when the other conditions were satisfied. (v) Microscopic examination disclosed the same general action before noticed as occurring between iron and its impurities: the iron went into solution around the impurity. Manganese sulphide on iron went into solution, and the iron also, while with manganese silicate and iron neither was attacked. Manganese and ferro-manganese went into solution on iron, which was unattacked, and even preserved. (vi) The presence of an impurity determines so many corrosion centres for iron, and so its influence depends more on quality than quantity; thus a more homogeneous iron, even if less chemically pure, may be more highly resistant to corrosion. (vii) Certain rapidly appearing corrosion centres in all irons examined were not visibly related to impurities recognised under the microscope.

The surface film on iron or steel, whatever its composition, may be much more homogeneous than the underlying metal and so lead to ambiguous statements as to the corrosibility of the material as a whole.

The effect of the carbon content on the corrosibility of iron is doubtless dependent very largely on the state of the carbon, and the amount of segregation in the metal, as well as the modifying effect of other elements. Experiments made by Heyn and Bauer (J. Iron and Steel Inst. 1909, I. 109) indicated that the corrosibility of a hard tool-steel (as measured by its rate of solubility in dilute sulphuric acid) was greatest when the quenching temperature was 400°.

Experiments made by a committee of the British Association appear to show that with pure iron-carbon alloys the maximum corrosibility corresponds to an all-pearlite iron with 0·89 p.c. of carbon.

It appears to be established that silicon and nickel increase the resistance of iron to rusting, while the same effect is claimed for small quantities of chromium, copper and phosphorus. Sulphur is generally admitted to stimulate rusting inasmuch as manganese sulphide, in which form the sulphur is usually present, generates the sulphate and indirectly ferrous sulphate. According to Stead (J. Iron and Steel Inst. 1901, I. 193) it is a recognised fact that the higher the proportion of sulphide of manganese in steel, the more liable is it to corrosion.

Influence of dissolved substances on rusting. The effect of dissolved salts in the water has received great attention in both the laboratory and industrial study of rusting.

It is now customary to classify dissolved substances as 'stimulators' or 'inhibitors.' As a general rule, a dissolved salt would be expected to stimulate corrosion by increasing the conductivity of the water. If the substance gives an acid solution this action will be all the more marked. On the other hand, strong salt solutions do not dissolve oxygen to the same extent as pure water, so that if the metal is completely immersed, retardation of rusting might be expected on this account. The above conclusions are borne out by the experimental work which has been done. Acids and ammonium salts stimulate corrosion very considerably, sodium chloride stimulates in dilute solutions and retards in concentrated solutions. Generally speaking, as the concentration is increased the corrosibility increases to a maximum (critical concentration), and then, unless interrupted by saturation of the solution, falls practically to zero (limiting concentration). The limiting concentration in certain cases is found to have an extremely low value, *e.g.* in alkaline solutions and in chromates and dichromates. Chromates and dichromates, and other oxidising agents are known to render iron passive, and Dunstan and Hill (*l.c.*) have shown that alkalis also produce passivity, so that the effects may all be due to this cause. In any case there is no doubt that above a small concentration, many substances, such as potassium and sodium hydroxides, carbonates, permanganates, iodates, chromates, and dichromates, borax, &c., will prevent rusting entirely. This property of potassium dichromate is beginning to find industrial application in the painting of iron work, and the protection of boilers. When more than one electrolyte is present in the water the effects are more complicated and it is found that the concentration of the inhibitor must usually be considerably greater than when it is present alone, if corrosion is to be prevented. An interesting special case is the behaviour of potassium dichromate in the presence of other salts. In such cases the dichromate being an acid salt reacts with the other salt to produce free acid, which destroys the passivity and allows rusting unless the dichromate is in large excess. For practical application as a rust preventive in such cases, potassium chromate which produces no acid is equally effective (Friend and Brown, J. Iron and Steel Inst. May 1911).

The action of sea water on iron is known to be much more vigorous than that of fresh water. In particular, owing to the action of such salts as magnesium chloride, the solution of the iron will take place even in the absence of air.

It has already been indicated that the concentration of dissolved oxygen at the surface of the metal has a very important influence on the progress of rusting. Practical experience confirms this in many ways. Pipe lines conveying water have been known to fail mainly on account of the extreme aeration of the water. Bridge structures always rust most readily near the water level, particularly if the water is in slight motion (*see* Cobb, *l.c.* 174–5 and Fig. 5). Iron work, which is deeply immersed in water or deeply buried, rusts much more slowly than that which is nearer to the atmosphere. The oxygen used up at the metal-water surface, is gradually replaced by diffusion from the air-water surface, and anything which prevents or decreases the rate of diffusion, such as reduction in the size of air-water surface, or covering it with a layer of material impermeable to oxygen, will delay rusting. The rate of flow of the water past the metal might be expected to have an influence in this respect, and Heyn and Bauer (Mitt. Königl. Material-prüfungs amt, 1910, 28, 93) have actually found that slight motion increases the rate of corrosion for both cast-iron and steel, especially the former. With an increased rate of flow, however, the corrosion decreased again. At high temperatures, it is naturally found that the tendency to rust is greatly increased although, under many conditions, this may be compensated for by the diminution in the supply of oxygen caused by the lower solubility.

In addition to lack of homogeneity in the metal itself it must be remembered that contact with a less electro-positive metal, the presence of small quantities of mill scale (Fe_3O_4), or even of rust itself, will cause the iron to become the soluble electrode in a galvanic circuit and thereby hasten its corrosion. It is therefore always advisable to avoid making contacts with other metals, or even with other kinds of iron, at points where electrolytic action might take place. The fact that iron in constant use does not corrode so fast as when at rest has been ascribed to the fact that any oxides formed are quickly removed and do not remain to exercise a galvanic influence. It may be remarked that rust itself, being porous and hygroscopic, offers additional favourable conditions for the continuation of rusting, quite apart from its galvanic effect.

Prevention of rust. Where the use to which iron is to be put does not admit of any protective coating, it is obviously necessary to consider all the above questions, with a view to providing conditions which shall keep corrosion as slow as possible. The steel plates of a steam boiler, for instance, are subjected to very stringent conditions which often cause extensive pitting, so that special attention has to be given both to the metal of which the boiler is contained and to the feed water. An example is described by Huntley (J. Soc. Chem. Ind. 1909, 28, 339) of remarkable corrosion in a stand-by boiler which could not be prevented by adding alkalis to the water. Blisters were found near the water level of the boiler, filled with a liquid which contained ferrous sulphate and sulphuric acid. The production of the sulphuric acid was found to be due to the presence of manganese sulphide in the steel. The blister of rust had retained the sulphuric acid, and oxygen passed in to oxidise the sulphide more rapidly than sodium hydroxide to neutralise the resulting acid. In this case, a remedy was effected by the addition of sodium arsenite, which presumably acted as a reducing agent and seized the dissolved oxygen. There are various other devices for the removal of oxygen, such as passing the feed water over scrap iron in a closed box, or the addition of an alkaline solution of tannin, which in the boiler forms strongly reducing pyrogallate. The use of dichromates or chromates has already been referred to, although the practice has not yet been widely tested on the large scale. Other attempts to protect iron have been made by placing pieces of zinc in contact with the metal so that the iron would be protected at the expense of the zinc. This practice is not very economical, and usually the effect of the zinc is confined to its immediate locality. In certain circumstances, however, the method is of value. A method of preventing or retarding the corrosion of boilers consists in applying an external current so that the boiler shell is the cathode, an immersed piece of wrought iron the anode, and the boiler-water the electrolyte. A current of 1 to 2 amperes at 4 to 8 volts. pressure is said to show a satisfactory reduction in the extent of the attack on the plates (Harker and Macnamara, J. Soc. Chem. Ind. 1910, 22, 1286).

Where conditions permit it, and especially in the case of structural iron work, it is of course a matter of economy to give to exposed iron work a protective coating. The first essential is to provide a coating which shall be as impervious as possible to air and water. Further considerations arise particularly with regard to the course of events at points where the coating has given way. For small articles a film of vaseline, black lead, or similar material which can be readily renewed is of great practical value. A coating of hot tar or pitch (Angus Smith) has also found wide application. Wire and articles of sheet metal may be protected by means of a coating of a less corrosible metal, usually zinc or tin. Tin plate finds its widest application in the manufacture of vessels to contain foodstuffs, and other articles for which a long life is not desired. It is not suitable for severe conditions, since at any point where the iron has become exposed a couple is produced in which the more electro-positive iron acts as the soluble electrode and suffers rapid corrosion. It is therefore of importance that the tin should be as free from pin holes as possible, and the ferroxyl indicator applied in a thin layer to the surface of the metal is a very valuable indication of the extent to which they exist. Every pinhole is indicated by the development of a blue spot which shows that iron is passing into solution. In galvanised or zinc-coated iron the state of affairs is reversed. The zinc protects the iron first by its own resistance to corrosion and then when the coating is broken, by the fact that the iron is protected at the expense of the more electro-positive zinc. There are several methods now in use for providing the zinc coating in the most suitable form. In the hot dip method the iron after passing through a ‘ fluxing solution ’ is dipped into molten zinc. The fluxing solution which has for its object the cleaning of the iron surface usually contains hydrochloric acid and the traces of this which are carried over often have an undesirable effect in producing corrosion of the finished product. In addition to the care necessary to avoid this effect, it is very important to control the bath so that a sufficiently uniform and thick layer of zinc shall be produced on the iron. Other methods of depositing the zinc are by electrolysis and by exposure to the vapour of zinc (Sherardising), and it is claimed that both these methods produce a more resistant coating than the hot dip process. The uniformity of a zinc coating can be tested by dipping the metal in a hot concentrated solution of caustic soda (Walker, Proc. Amer. Soc., Testing Materials, 1909, 8, 430). Pure zinc, under such conditions, is practically unaffected, but in contact with iron, as it would be where there were cracks or pinholes in the coating, a current of hydrogen is produced from the iron. Tested in this way, hot galvanised iron was found by Walker to be relatively free from imperfections, but wet or electrolytically galvanised was frequently porous, indicating the necessity for careful supervision of the rate of deposition of the zinc so as to obtain the most adherent coating. A number of other protective devices, mostly patented, depend upon the production from the iron itself of a resistant surface layer. The best known of these is the Barff-Bower method of producing a fine closely adhering layer of magnetic oxide, by the action of steam on the heated metal. In this way a very uniform and durable coating can be obtained on articles which are not too large. When the metal does become exposed, however, the oxide forms with the metal a couple which results in stimulated corrosion of the iron. In the Tatlock process, the magnetic oxide is obtained by heating in a bath of fused sodium or potassium nitrate. The Coslett process, which is largely used in bicycle manufacture, depends on the production of an insoluble layer of phosphate by the regulated action of phosphoric acid. These and similar methods of protection are all fairly efficient for the protection of smaller articles or sheets of iron under not too stringent conditions. But where, as is often the case with structural and massive ironwork, the water may contain much soluble foreign matter (often of an acid nature), the progress of corrosion must be carefully watched and checked. This involves the use of a protective coat which shall be renewable *in situ* and easily applied. For this reason, a considerable amount of attention is now being paid to the protection of iron work by paint, and the relative values of the various pigments and media. It is again desirable, in the first place, that the film shall be impervious and mechanically durable; and secondly, that when its protective action breaks down the subsequent effects should be inhibitive rather than stimulative. Since oil does not penetrate iron, special attention has to be paid to the adhesiveness of the first coat, and therefore to the thorough scraping and cleaning of the iron surface before it is applied. In addition to this it is of very great importance that the metal should be absolutely dry. It is also necessary to pay special attention to the purity and homogeneity of the material, especially to the freedom of the linseed oil from resins. With regard to the effect of the pigment itself a great deal of important testing work on the large scale is now in progress in America under the direction of the American Society for Testing Materials and the Paint Manufacturers' Association of the United States. A full account of these experiments and a general discussion of the protection of iron is to be found in Cushman and Gardner's Corrosion and Preservation of Iron and Steel.

Cushman (Bull. 25, U.S. Dept. of Agric. 1909), as a result of small scale experiments, has divided pigments into three classes, inhibitors, indeterminates, and stimulators. In the first class are found (probably on account of their passivifying properties), the various chromate pigments containing zinc, lead, and barium chromates. The value of these inhibitors appears to be confirmed by the earlier observations of the large scale tests. On the other hand, good conducting pigments such as graphite are almost invariably found to be stimulators.

Another important aspect of the corrosion problem is the possible rusting of steel imbedded in concrete. If this took place to any great extent the consequent increase in volume would speedily lead to the destruction of the concrete with disastrous results. It is generally believed, however, that concrete, properly prepared, is almost a perfect preservative for steel, the excess of alkali exercising a pronounced protective action. It is obviously necessary, however, if preventive conditions are to be maintained, that the mortar should be dense and well rammed, so that the percolation of water, carrying away lime, and possibly introducing stimulative dissolved matter, shall be avoided. An even more dangerous contingency, so far as concrete is concerned, is the possibility of corrosion being stimulated, under otherwise preventive conditions, by stray electric currents which, in the modern development of electrical industry, have been so fruitful a source of the corrosion of underground pipe lines.

From the economic point of view the question of rust prevention presents itself as one needing large scale experiments for its proper study. The numerous conditions which affect the corrosion of unprotected iron, and the various effects of protecting agents under different conditions render all suggested acceleration tests of little value. The ferroxyl test and the rate of solution in dilute acid, although they give valuable information, do not reproduce industrial conditions at all satisfactorily, and any conclusions obtained from them must be applied with caution. A. Sm.

RUTHENIUM. Sym. Ru. At.wt. 101·7. This metal is obtained, together with osmium, as a by-product in the treatment of osmiridium and other native alloys of the platinum metals.

The residue from the extraction of iridium and osmium is treated with a mixture of potash and potassium nitrate in a silver crucible. After cooling, the brown mass is extracted with water, an orange solution of potassium ruthenate being formed. It is separated by decantation and the ruthenium salt is precipitated by means of nitric acid or alcohol. It is washed, dried, and reduced by hydrogen. The metal thus obtained, which is impure, is again melted with potash and nitre; it is then treated with chlorine, when volatile ruthenium peroxide is formed, which is redistilled with water in a current of chlorine. The peroxide is then converted into oxide or sesquichloride, which when reduced with hydrogen gives the pure metal (Claus, Ann. Chim. Phys. 1860, [iii.] 59, 111). The metal may be obtained crystalline by heating its alloy with tin in a carbon crucible, in a current of hydrogen chloride, or by heating the finely-divided metal with pyrites and borax (*v.* Deville and Debray, Compt. rend. 1879, 89, 590).

Ruthenium is white, hard, and brittle, and, after osmium, is the least fusible but the most readily oxidised metal in the group. The fused metal has a sp.gr. of 12·06 and is scarcely attacked by acids or even by *aqua regia.*

At a bright red heat it is oxidised superficially by air or oxygen. It is also attacked by chlorine and by fluorine, but not by sulphur.

In a fine state of division the metal has energetic catalytic properties.

Colloidal ruthenium has been obtained in the same manner as colloidal osmium (*v.* OSMIUM).

Neither the metal nor its salts have found any definite application in the arts, although a small quantity, probably for chemical uses, is reported officially as having been imported into the United States in 1910.

RUTHENIUM COMPOUNDS.

Ruthenium forms the oxides Ru_2O_3, RuO_2, RuO_4, and salts corresponding to the oxides RuO_3, Ru_2O_7 (Gutbier and Ransohoff, Zeitsch. anorg. Chem. 1905, 45, 243).

Ruthenium sesquioxide Ru_2O_3 forms a black scaly mass, produced when the trioxide is heated in carbon dioxide. The corresponding trihydroxide $Ru(OH_3)$ is obtained by precipitating the trichloride with an alkali. It is a black-brown precipitate insoluble in water and alkalis, but forming a yellow solution in acids.

Ruthenium dioxide RuO_2 is obtained by roasting the disulphide or sulphate in air or by heating osmiridium alloy in a current of pure air, when the dioxide is carried forward by the osmium tetroxide formed at the same time, and deposited in the colder part of the tube; the osmium tetroxide being more volatile is carried further. The dioxide crystallises in small hard tetragonal pyramids, possesses a green metallic lustre, a bluish-green iridescence, and is isomorphous with *cassiterite* and *rutile.* The hydroxide $Ru(OH)_4,3H_2O$ is a red-brown substance giving yellow solutions in alkalis and acids.

Ruthenium tetroxide RuO_4 is prepared by treating a solution of potassium ruthenate (formed by fusing the element with sodium peroxide; or, better, with potash and potassium nitrate) with chlorine (Mylius and Dietz, Ber. 1898, 31, 3187; Gutbier, Zeitsch. angew. Chem. 1909, 22, 487). It forms beautiful crystals, fairly stable when dry, but decomposing rapidly when moist. Its vapour has an irritating smell and is poisonous. It blackens organic matter, and is reduced by alcoholic potash. When the solid tetroxide is treated with alcohol serious explosions may occur (Debray and Joly, Compt. rend. 1891, 113, 693).

Ruthenium dichloride $RuCl_2$ is probably present in the blue liquid obtained by the action of sulphuretted hydrogen on the *trichloride* $RuCl_3$, which is best prepared by treating the tetroxide with 20 p.c. hydrochloric acid, and then placing the whole in a cooling mixture under reduced pressure for 2 hours. It forms an almost black, crystalline mass, and yields an orange-coloured solution in water, which when warmed gently deposits an intensely black precipitate (Gutbier and Trenkner, Zeitsch. anorg. Chem. 1905, 45, 166, 178). The solid chloride becomes liquid when in contact with the air and dissolves in dilute aqueous or alcoholic hydrochloric acid with an intense purple-red colour (Gutbier, *l.c.*). The trichloride forms double salts with alkali chlorides, known as *rutheniochlorides* or *chlororuthenites* (Miolati and Tagiuri, Gazz. chim. ital. 1900, 30, ii. 511; Howe, J. Amer. Chem. Soc. 1901, 23, 775; *ibid.* 1904, 26, 543, 942).

Ruthenium tetrachloride $RuCl_4$ has not been obtained pure; it also forms double chlorides with the alkali chlorides and with hydrochlorides of organic bases, known as *ruthenichlorides* or *chlororuthenates* (Gutbier and Zwicker, Ber. 1907, 40, 690). Bromide and iodide derivatives of ruthenium are also known.

Ruthenium sulphide Ru_2S_3 occurs naturally as the mineral *laurite* and crystallises in small octahedra (*see* Antony and Lucchesi, Gazz. chim. ital. 1900, 30, ii. 539).

Ruthenic sulphate $Ru(SO_4)_2$ is obtained by dissolving the tetrahydroxide in sulphuric acid. It forms a deliquescent powder closely resembling mosaic gold. It gives a red-yellow solution in water, which when treated with sulphur dioxide changes from bright red to green, then to blue. When alcohol is added to this blue solution colloidal *ruthenium sulphite* $Ru_2(SO_3)_3$ is precipitated (Antony and Lucchesi, *ibid.* 71). By the continued action of sulphur dioxide on ruthenic sulphate, *Ruthenium dithionate* RuS_2O_6 is formed (*ibid.* 1898, 28, ii. 139).

Ruthenium nitrosochlorides and some of its complex derivatives are described by Howe (J. Amer. Chem. Soc. 1894, 16, 388); Lind, (*ibid.* 1903, 25, 928); Brizard (Compt. rend. 1899, 129, 216; Ann. Chim. Phys. 1900, vii. 21, 311).

Ruthenium forms complex compounds with ammonia (Werner, Ber. 1907, 40, 2614). *Rutheniocyanides* corresponding with the ferrocyanides and *rutheniocyanic acid* are described by Howe (J. Amer. Chem. Soc. 1896, 18, 981; Howe and Campbell, *ibid.* 1898, 20, 29); ruthenium carbonyl compounds by Mond, Hirtz and Cowap (Chem. Soc. Trans. 1910, 798).

Ruthenium silicide RuSi, forms hard, small white crystals of sp.gr. 5·40, (Moissan and Manchot, Compt. rend. 1903, 137, 229).

Ruthenium phosphorus halides have been obtained by Strecker and Schurigin (Ber. 1909, 42, 1767). Z. K.

RUTILE. A native form of titanium dioxide (TiO_2) crystallising in the tetragonal system and isomorphous with cassiterite (SnO_2). Other native forms of titanium dioxide are the less common and less stable minerals anatase and brookite. Rutile forms prismatic crystals with a good prismatic cleavage. It is translucent to opaque, often with a brilliant lustre, and ranges in colour from reddish-brown to black; the streak is yellowish-brown; H. 6–6½. The characteristic reddish-brown colour (hence the name rutile, from the Latin *rutilus*, red) may usually be seen on thin cleavage flakes when the mineral is broken. The range in colour, and also in sp.gr. (4·2–5·2), is due to the presence of variable amounts of ferric oxide, apparently in solid solution in the rutile; in the black variety, called *nigrine*, this may be as high as 10 p.c. Rutile occurs in granitic rocks, but more frequently in gneiss and schist, and is often collected in quartz veins traversing these rocks. Being resistant to weathering agents, it accumulates in sands and clays. Large crystals are found in quartz veins at Graves Mountain in Georgia, in the apatite mines at Kragerö in Norway, at Risör in Norway, &c. At Roseland in Nelson Co., Virginia, it occurs abundantly in pegmatite, and together with apatite, &c., forms a dyke-rock called nelsonite (W. M. Thornton, Amer. J. Sci. 1911, 31, 218). These rocks are quarried, crushed, and washed, and the rutile obtained in the form of a resinous brown sand. Small amounts of the mineral are also produced commercially in Norway. It is used in the manufacture of cast-iron and cast-steel; for imparting a yellowish tinge of colour to porcelain (particularly for false teeth); in dyeing leather; and in the 'carbons' of electric arc-lights. L. J. S.

RUTIN *v.* Glucosides.

RYE *v.* Cereals.

S

SABADILLA *v.* *Veratrine*, art. Vegeto-alkaloids.

SABINENE *v.* Terpenes.

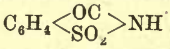
SABROMIN. Trade name for the calcium salt of dibromobehenic acid, which is obtained by the action of bromine on erucic acid (*v.* Synthetic drugs).

SACCHARANE is obtained by heating sugar *in vacuô* at 200°, and extracting the caramelised mass with methyl alcohol until the solvent is no longer coloured, treating the insoluble residue with water, and evaporating the solution *in vacuô*, after filtration. The yield is about 20 p.c. of the sugar taken. Saccharane, which has the formula $C_{12}H_{22}O_4,2H_2O$, is not precipitated by lead acetate, and is non-hygroscopic and tasteless. As its solution has a constant colouring power it has been proposed to employ it as the standard for determining the colour-value of commercial caramels by colorimetric methods (*v.* Caramel) (Ehrlich, J. Soc. Chem. Ind. 1910, 506).

SACCHARIC ACID *v.* Carbohydrates.

SACCHARIMETRY *v.* Sugar.

SACCHARIN (o-*Benzoicsulphinide*)



$$C_6H_4{<}\genfrac{}{}{0pt}{}{OC}{SO_2}{>}NH$$

was discovered by Remsen and Fahlberg in 1879 (Ber. 12, 469; Amer. Chem. J. 1, 426), and was first prepared by Fahlberg on a large scale from coal tar or analogous substances containing a large proportion of toluene, benzene, &c.

Preparation.—Toluene, or the substance containing it, is heated with fuming sulphuric acid, whereby *o*- and *p*-sulphonic acids

$$CH_3{\cdot}C_6H_4{\cdot}SO_3H$$

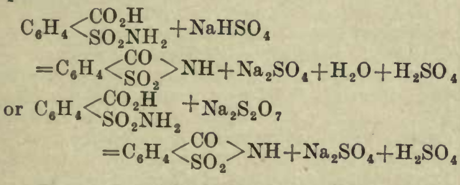
are formed. These are converted into their calcium salts by treatment with calcium carbonate and from the calcium salts the sodium salts are obtained. The latter are dried, and treated with phosphorus trichloride and a stream of chlorine, whereby two sulphonic chlorides are formed. The phosphorus oxychloride also formed is distilled off and the residue is strongly cooled and centrifugalised when the crystalline para- chloride separates from the ortho- chloride which is liquid. The latter is treated with dry ammonia or ammonium carbonate forming the amide $CH_3{\cdot}C_6H_4{\cdot}SO_2NH_2$, which is washed with water and on oxidation with alkaline potassium permanganate yields the potassium salt of *o*-sulphamine benzoic acid; the latter is treated with hydrochloric acid, forming the free acid $CO_2HC_6H_4SO_2NH_2$, which is spontaneously converted into saccharin (Eng. Pats. 6626, 1885; 22787, 1891; 10955, 1895; 17401, 1896; 9962, 1899; D. R. P. 122567).

A number of other methods of preparing saccharin have been proposed.

100 lbs. of *o*-toluene sulphonamide may be mixed with 23 lbs. of slaked lime and stirred with 200 gallons of water. The mixture is heated to 70°–80°, and 180 lbs. of 98 p.c. calcium permanganate dissolved in 50 gallons of water are added gradually with constant stirring. The manganese compounds are removed by filtration and the saccharin is precipitated from the filtrate by addition of acid (Eng. Pats. 3563, 25481, 1903; *see* also Eng. Pats. 3680, 1898; 4525, 1900; 22214, 1901; U.S. Pat. 692863, 1902); or the *o*-toluene sulphonamide may be converted into saccharin by oxidising it electrolytically in the presence of alkaline permanganate at 40°–50° (Eng. Pat. 9322, 1903; *see* also Eng. Pat. 8661, 1895).

The methyl group in toluene may be oxidised to carboxyl before the introduction of the sulpho- or sulphamino- group, thus avoiding the formation and subsequent separation of *p*-toluene sulphonic chloride (Eng. Pat. 14122, 1906).

Saccharin may be manufactured by heating 10 parts of *o*-sulphamine benzoic acid dissolved in 50 parts of alcohol with 40 parts of sodium bisulphite or 20 parts of sodium pyrosulphate for several hours on a water-bath with a reflux condenser when the following reaction takes place :—



$$C_6H_4{<}\begin{matrix}CO_2H\\SO_2NH_2\end{matrix}+NaHSO_4$$
$$=C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NH+Na_2SO_4+H_2O+H_2SO_4$$
$$\text{or } C_6H_4{<}\begin{matrix}CO_2H\\SO_2NH_2\end{matrix}+Na_2S_2O_7$$
$$=C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}NH+Na_2SO_4+H_2SO_4$$

The sulphuric acid is neutralised, the alcohol removed by distillation, when the residue consists of saccharin and its ethyl ester, which is readily hydrolysed by sodium hydroxide at the ordinary temperature. The yield is said to be 95 p.c. of the theoretical (Eng. Pat. 7199, 1900; *see* also Eng. Pats. 3930, 1895; 21026, 1896; 1164, 15009, 1897; 19629, 1899; 12585, 1900).

Saccharin has also been prepared from *o*-benzaldehyde sulphonic acid (Eng. Pat. 27655, 1896) and from *p*-bromacetanilide (Kreis, Annalen, 1895, 286, 377). For other methods (*see* Witting, Chem. Zeit. 11, 314; Eng. Pats. 5135, 1895; 1956, 1896; 10810, 1897; 6537, 1901; U.S. Pat. 692598, 1902; List and Stein, Ber. 1898, 31, 1665).

Commercial saccharin generally contains a fairly large proportion of *p*-sulphamine benzoic acid, the sweetening power of which is far less than that of saccharin.

To purify it, hydrochloric acid sufficient to neutralise the *p*- salt is added to a concentrated solution of the alkali salts of crude saccharin. The para- acid separates, leaving the ortho- salt in solution which may now be treated with acid to obtain pure saccharin (Eng. Pat. 22787, 1891; 10769, 21417, 1903).

Saccharin is obtained in a very pure form by crystallisation from acetone, when it forms large, transparent monosymmetric crystals, which, when crushed, exhibit phosphorescence (Pope, Chem. Soc. Trans. 1895, 985).

Properties.—Saccharin is a white crystalline substance which, when quite pure, melts at 220°, and is 500 times as sweet as sugar (the commercial product is about 300 times as sweet), 1 part in 10,000 of water giving an intensely sweet taste. It sublimes at 100° and is soluble in cold water only to the extent of 1 in 400, in boiling water 1 in 28, in alcohol 1 in 30, in glycerol and in amylacetate 1 in 50, in ethyl acetate 1 in 20. It is also soluble in ether, in ammonia, and in alkali carbonate solutions, the alkali salts being formed in the latter case. It is not attacked by nascent hydrogen in alkaline solutions, by potassium permanganate, by hydrogen peroxide or by halogen or nitric acid in the cold. With hot nitric acid it is hydrolysed.

When boiled with hydrochloric acid it forms *o*-sulphamino benzoic acid, and then ammonium hydrogen sulphobenzoate $CO_2H{\cdot}C_6H_4{\cdot}SO_3NH_4$ (Remsen and Burton, Amer. Chem. J. 11, 403).

Saccharin acts as a disinfectant, but as a preservative for beer it is said to be practically useless (Burkard and Seifert, Chem. Zeit. 1895, 19, 220; Machledeit, Wochenschr. Brauerei, 1898, 15, 365).

Saccharin is used as a sweetening agent, particularly in the manufacture of sweetened aerated waters (Chem. Zeit. 12, 106; Bull. Soc. chim. 1889, 348; Levinstein, J. Soc. chem. Ind. 1886, 75), although its use in food is prohibited in some countries. It is employed in medicine as a substitute for sugar in diabetes, liver disease, for the reduction of corpulence, and generally where the use of sugar is undesirable, and it may be mixed with alkaloids to render their taste less objectionable (Eng. Pat. 596, 1886).

According to Nencki (Chem. Zeit. Rep. 1899, 23, 372), and to Berlioz (*ibid.* 1900, 24, 416), the effect of saccharin on the digestion is less than that of an equivalent weight of sugar. This opinion is, however, contrary to the widely accepted view and is, according to Windisch (Wöch. Brau. 1900, 17, 284), based on essentially incorrect assumptions (*see* also Chassevant, Compt. rend. Soc. Biol. 1901, 53, 206; J. Soc. Chem. Ind. 1886, 421; *ibid.* 1882, 292, 688; *ibid.* 1889, 66; *ibid.* 1890, 545, 1062; Thümen, Chem. Zeit. 1891, 15, 634).

Tests.—Saccharin gives a voluminous precipitate with mercurous nitrate and a less abundant precipitate soluble in excess with mercuric nitrate (Parmeggiani, Bull. chim. Farm. 1908, 47, 37). When saccharin is heated with sulphuric acid and diresorcinol a product is obtained which when treated with water and filtered forms an intensely violet liquid (Wauters, J. Soc. Chem. Ind. 1909, 733). Saccharin is evaporated to dryness with nitric acid, cooled, and a few drops of a solution of sodium hydroxide in 50 p.c. alcohol is added, a faint yellow colour is formed. If the liquid is spread out on the surface of the dish and heated rapidly, blue-violet and red streaks are formed (Lindo, Chem. News, 1888, 58, 51, 155). The substance containing saccharin is evaporated to dryness and transferred to a small reduction tube in which a small piece of sodium or potassium has been placed. The whole is heated, and when the reaction is over, the tube, whilst still hot, is immersed in freshly prepared sodium nitroprusside when a violet colour will be produced—salicylic acid does not interfere with this test (Mahler, Chem. Zeit. 1905, 29, 32).

The substance is evaporated almost to dryness in a porcelain crucible, and the residue, after being treated with a drop or two of water and a particle of caustic soda, is again evaporated to dryness and fused. The cold melt is dissolved in 1 c.c. of water neutralised with dilute acid and tested with 1 p.c. ferric alum reagent, when, if saccharin is present, a violet colour is produced (Geuth, Amer. J. Pharm. 1909, 81, 536; *see* also Truchon, Chem. Zentr. 1900, i. 691; Brévans, *ibid.* 1105; Villiers, *ibid.* 1904, i. 1457; Chase, J. Amer. Chem. Soc. 1904, 26, 1627).

If salicylic acid is present it has to be removed before this test can be applied; for this purpose the solution is mixed with hydrochloric acid and bromine water is added in excess, this precipitates the salicylic acid quantitatively. The solution is then filtered and excess of bromine is removed by a current of air (Hairs, Chem. Zentr. 1893, ii. 987; Bonamartini, Rev. Intern. Falsif. 1906, 19, 39).

When saccharin is heated with a small quantity of a mixture of 5 c.c. of phenol and 3 c.c. of strong sulphuric acid for 5 mins. at 160°–170°, and the product is dissolved in water, on addition of a solution of sodium hydroxide, the solution becomes purple-red or rose-red according to the amount of saccharin present: salicylic and benzoic acids do not interfere with this reaction. Other phenols also give characteristic colours (Kastle, Chem. Zentr. 1906, i. 1575).

A few grams of the substance is dissolved in 10 c.c. of water and made faintly alkaline. A solution of *p*-diazonitraniline is added drop by drop with agitation until the colour first formed disappears. The liquid is then shaken up with ether and the lower layer is withdrawn and replaced by 20–30 drops of 10 p.c. caustic soda solution. On gentle agitation a green ring is formed in the presence of saccharin, a red one in that of salicylic acid, and a red-brown ring in the presence of both. If the soda is removed and replaced by ammonia, the ether is decolourised and the ammonia becomes blue-green in the first case, red in the second, and violet in the third case (Riegler, Chem. Zentr. 1901, i. 66).

Saccharin may be determined microchemically by means of nitron, if the former be first converted into *o*-sulphamino benzoic acid by treatment with dilute alkali (Visser, Chem. Zentr. 1907, i. 302).

To detect saccharin in beer, wines, syrups, &c., the bitter principle of hops must first be removed by treatment with copper nitrate until no further precipitate is formed. The solution is then mixed with pure sand and phosphoric acid, and after concentration is extracted with a mixture of ether and light petroleum. The extract is evaporated and the residue is dissolved in a little sodium carbonate, and is tested by the taste and other methods as above. If the substance contains tannin it may be removed by the addition of ferric chloride, after which the solution is made slightly alkaline by addition of calcium carbonate.

The solution of the food or beverage may be freed from alcohol by evaporation and acidified with acetic acid (20 drops for every 100 c.c.); it is then treated with a normal solution of lead acetate in excess and allowed to stand for 30 minutes, after which excess of N/5 solution of sodium sulphate containing an equal quantity of sodium phosphate is added and the lead salts are removed by filteration. The filtrate is concentrated on the water-bath, acidified with dilute sulphuric acid and shaken with a mixture of equal volumes of ether and benzene. The extract after evaporation may now be treated with potassium permanganate and sulphuric acid to oxidise the salicylic acid, and the product again extracted with ether and benzene. The evaporated extract is then treated as above (Bianchi and Nola, J. Soc. Chem. Ind. 1909, 1267; Jörgensen, *ibid.* 732; Pawlowski, *ibid.* 732).

For other methods of detecting saccharin in beverages, *see* Spaeth, Zeitsch. angew. Chem. 1893, 579; Wauters, Chem. Zentr. 1896, i. 576; Morpurgo, *ibid.* 1897, ii. 531; Rossing, *ibid.* 1899, ii. 274; Herzfeld and Wolff, Wochenschr. Brau. 1898, 15, 335, 608; Wirthle, Chem. Zeit. 1900, 24, 1035; Blarez, Bull. l'Assoc. Chim. Sucr. Dist. 1899, 17, 319; Boucher and Bounge, Bull. Soc. chim. 1903, [iii.] 29, 411; Spica, Gazz. chim. ital. 1901, 31, ii. 41; Tagliavini, Boll. Chim. Farm. 1907, 46, 645.

To detect saccharin in foods rich in proteids, fats, and starch, the substance, mixed with sand and slaked lime, may be extracted with a mixture of alcohol and sodium chloride solution. The fat is then removed from the extract by light petroleum, and the remaining liquid is freed from alcohol by evaporation on a water-bath, cooled, extracted with ether to remove dulcin, again evaporated and acidified with sulphuric acid, after which the saccharin is extracted with a mixture of ether and light petroleum (Tortelli and Piazza, Zeitsch. Nahr. Genussm. 1910, 20, 489).

For the detection of saccharin in milk and butter, *see* also Leys, Compt. rend. 1902, 132, 1056; Wirthle, Chem. Zeit. 1901, 25, 816; Formenti, Chem. Zentr. 1902, ii. 541.

For the detection and estimation in cocoa powders, Driessen, Mareeuw, Pharm. Weekblad. 1907, 44, 245.

Saccharin may be estimated by the following process:—

0·5–1 grm. of saccharin or saccharin mixture is weighed into a 100–120 c.c. glass flask and 50 c.c. of N/1,HCl is added. The flask, fitted with an air condenser, is boiled gently for 2½ hours, the ammonia produced is estimated by Kjeldahl's process, and the number of c.c. N/10 sulphuric acid used to neutralise the ammonia multiplied by 0·0183 gives the weight in grams of pure saccharin present in the sample (Proctor, Chem. Soc. Trans. 1905, 242; Testoni, Zeitsch. Nahr. Genussm. 1909, 18, 577). Pure saccharin should yield 7·65 p.c. of ammonia. Saccharin may also be estimated as mercury saccharinate $(C_6H_4[COSO_2]N)_2Hg$ by precipitating with mercury nitrate (Vitali, Chem. Zentr. 1899, i. 1297). For other methods, *see* (Delle, *ibid.* 1900, ii. 744; Défournel, J. Pharm. 1901, [iv.] 13, 512; Parmeggiani, *l.c.*), in urine and fæces (Bloor, J. Biol. Chem. 1910, 8, 227; Wakeman, *ibid.* 233).

The chief impurity in commercial saccharin, *p*-sulphaminobenzoic acid, may be estimated by titration with N/10 caustic soda (Glücksmann, Chem. Zentr. 1901, ii. 588; *see* also Reid, Amer. Chem. J. 1899, 21, 461; J. Soc. Chem. Ind. 1900, 860).

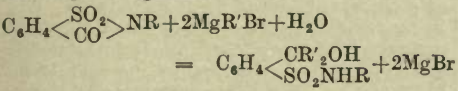
DERIVATIVES OF SACCHARIN.

Saccharin combines with mineral and organic bases, forming well-defined, usually crystalline salts which may be obtained by the action of carbonates or bicarbonates on saccharin or by the action of sulphate on *sodium saccharinate*, which is very soluble in water and is known as *soluble saccharin.* The latter is often used instead of saccharin, both in medicine and for sweetening purposes (Chemist and Druggist, 32, 642).

Sucramine, the ammonium salt, is formed by dissolving saccharin in the required amount of ammonia. After standing for some time, the solution deposits white crystals far sweeter than saccharin, being 700 times as sweet as cane-sugar. It melts at about 150°, is equally soluble in hot and cold water, and is also soluble in methyl and ethyl alcohol, but not in other organic solvents (Défournel, Bull. Soc. chim. 1901, 25, 322; Bellier, Chem. Zentr. 1901, i. 423; Blarez, Zeitsch. Nahr. Genussm. 1901, 4, 763). Other metallic derivatives are also known.

Alkyl derivatives of saccharin of the type $C_6H_4{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NR$ are obtained by the interaction of the sodium salt and the required alkyl iodide (Fahlberg and List, Ber. 1887, 20, 1596; Brackett, Amer. Chem. J. 9, 406).

Ethyl saccharin (Sachs, Wolff and Ludwig, Ber. 1904, 37, 3252) forms long needles, m.p. 93°–94°, is tasteless and readily soluble in hot water. Like other alkyl saccharins it combines with organomagnesium bromide thus:—



$$C_6H_4{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NR+2MgR'Br+H_2O = C_6H_4{<}\genfrac{}{}{0pt}{}{CR'_2OH}{SO_2NHR}+2MgBr$$

(Sachs, Wolff and Ludgwig, *l.c.*).

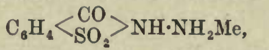
Methyl saccharin forms flat needles, m.p. 131°–132°. Methyl saccharin of formula

$$C_6H_3Me[COSO_2]NH$$

is formed by converting *p*-toluidine-*m*-sulphonic acid into the corresponding cyano- toluene sulphonic acid by the diazo- reaction. By the action of ammonia, the cyano sulphamide is obtained, and this by hydrolysis yields the acid $C_6H_3Me(SO_2NH_2)CO_2H$, which on heating yields methyl saccharin (D. R. P. 48583). It melts at 246°, resembles saccharin in taste, is readily soluble in hot, sparingly in cold, water, and is soluble in alkalis and many organic solvents. A number of derivatives of methyl saccharin have been obtained (Weber, Ber. 1892, 25, 1737).

Ethoxy saccharin $OEtC_6H_3{<}\genfrac{}{}{0pt}{}{SO_2}{CO}{>}NH$, has m.p. 257°–258°, and is not sweet (Remsen and Palmer, Amer. Chem. J. 8, 227).

Saccharinate of monomethylamine



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}NH{\cdot}NH_2Me,$$

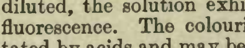
m.p. 156·5°–157°, is prepared by mixing aqueous solutions of methylamine and saccharin in equimolecular proportions and evaporating the mixture *in vacuô.* Salts of saccharin with other amines are prepared similarly. They are very soluble in water and in alcohol, but insoluble in most organic solvents (Fr. Pat. 322096, 1902; Eng. Pat. 12181, 1902).

Saccharin reacts with phenylcarbazide, forming a compound which crystallises in white needles, m.p. 98°, and is decomposed by dilute sulphuric acid or by prolonged boiling with water with formation of *o*-sulphaminobenzoic acid (Défournel, Bull. Soc. chim. 1901, [iii.] 25, 604).

Nitro-, *amino-*, and *alkylnitro-*, and *amino-* derivatives of saccharin have been prepared (Noyes, Amer. Chem. J. 8, 167; Remsen and Gray, *ibid.* 1897, 19, 496; J. Soc. Chem. Ind. 1889, 476; Eckenroth and Koerppen, Ber. 1896, 29, 1048; *ibid.* 1897, 30, 1265).

When chlorine is passed into a potash solution of saccharin the products formed depend on the quantity of alkali present. If an equivalent amount of saccharin is used, the sparingly soluble *chloride* $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{SO_2}{>}NCl$, m.p. 152°, separates. This substance is not sweet, is similar in taste to a hypochlorite and in odour to chloral. If excess of alkali is present, the solution remains clear, and if an acid is added a precipitate is formed which may be *o*-sulphonchloramidobenzoic acid or *o*-sulphondichloramidobenzoic acid or a mixture of both, depending on the quantity of chlorine used (Chattaway, Chem. Soc. Trans. 1905, 1882).

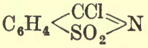
Saccharin forms a white waxy condensation product with formaldehyde (Parmeggiani, *l.c.*). It also combines with caffeine, strychnine, quinoline, piperazine, phenetidene, and antipyrine, forming products which are said to be useful as antiseptics and antifermentatives (Eng. Pat. 25152, 1899).

Saccharin condenses with phenols, forming products of a constitution similar in type to that of phthalein, thus with phenol, the product  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(C_6H_4OH)_2}{SO_2}{>}NH$ is formed; it dissolves in alkalis giving a red solution, which is decolourised on addition of acids. With resorcinol, a brown-red mass is obtained which forms an orange-yellow solution in alkalis. When diluted, the solution exhibits a powerful green fluorescence. The colouring matter is precipitated by acids and may be purified by dissolving it in alcohol and precipitating with water. It forms a brown resin with a metallic lustre and yields a *triacetyl-* derivative, m.p. 286°, which, on saponification, yields the pure *sacchareïn* $SO_2{<}\begin{smallmatrix}NH\\C_6H_4\end{smallmatrix}{>}C{<}\begin{smallmatrix}C_6H_3OH\\C_6H_3OH\end{smallmatrix}{>}O$. The latter crystallises in salmon coloured scales, m.p. 265°–267°, soluble in water, alcohol, and in alkalis, forming in the latter a pure yellow solution with a green fluorescence. It yields halogen derivatives which also form coloured solutions in alkalis. The sacchareïns of ethyl- and methylmetaminophenols also form colouring compounds (Monnet, and Kœtschet, Bull. Soc. chim. 1897, [iii.] 17, 690, 1030; Sisley, *ibid.* 821). The latter, although very similar to the rhodamines in colouring and general properties, are instantly decolourised by alkalis, but if an acid radicle is introduced in the imido- group, the colouring matters formed are among the most stable towards alkalis.

Pseudo - saccharin $C_6H_4{<}\begin{smallmatrix}C(OH)\\SO_2\end{smallmatrix}{\geqslant}N$ or $C_6H_4{<}\begin{smallmatrix}CNH\\SO_2\end{smallmatrix}{>}O$ is formed by heating equimolecular proportions of sulphobenzoic acid and acetonitrile at 165°–170° for 5 hours. The product is extracted with alcohol, and on evaporation of the latter, the ψ-saccharin separates as minute white crystals, m.p. 225°. They dissolve readily in water and in alcohol, not in ether, and are not sweet (Mathews, J. Amer. Chem. Soc. 1898, 20, 662).

Many derivatives of ψ-saccharin have been prepared (Jesurun, Ber. 1893, 26, 2286; Remsen, *ibid.* 2634; Fritsch, *ibid.* 1896, 29, 2295; Bradshaw, Amer. Chem. J. 1906, 35, 335).

Chloro-ψ-saccharin (*chlorobenzalsultim*)



$$C_6H_4{<}\begin{smallmatrix}CCl\\SO_2\end{smallmatrix}{\geqslant}N$$

is prepared by passing chlorine into an aqueous solution of saccharin. It forms white crystals, m.p. 170°, only sparingly soluble in most organic solvents and is converted by alcohol into *ethoxy-ψ-saccharin* (*ethoxybenzalsultim*) (Maselli, Gazz. chim. ital. 1900, 30, ii. 529; Fritsch, Ber. 1896, 29, 2290).

For other halogen derivatives, *see* Roode, Amer. Chem. J. 13, 217; Brackett, *l.c.*; Holleman, Rec. trav. chim. 1906, [ii.] 25, 330.

SACCHARINIC ACID $C_6H_{12}O_6$. An unstable acid obtained as the calcium salt by boiling solutions of saccharin with freshly precipitated chalk (Scheibler, Ber. 1880, 13, 2212; Kiliani, Annalen, 1883, 218, 373; Liebermann and Scheibler, Ber. 1883, 16, 1821; Hermann and Tollens, *ibid.* 1884, 17, 1333). *Iso-* and *metasaccharinic acids* are formed as calcium salts by the action of lime on milk-sugar. The former is also formed by boiling oxycelluloses with milk of lime (Faber and Tollens, Ber. 1899, 32, 2596). The latter may be prepared by treating galactose with water and freshly prepared calcium hydroxide Kiliani and Sandra, Ber. 1893, 26, 1650).

Para- saccharinic acid is also formed in the preparation of the *meta-* acid by the last method.

Both the *meta-* and the *para-* acids are readily converted into the same pentose—an aldose which when oxidised with bromine yields a bulanetriolcarboxylic acid (Kiliani, Ber. 1908, 41, 120).

Literature on the saccharinic acids and their derivatives: Lobry de Bruyn and von Ekenstein, Ber. 1895, 28, 3078; Fischer and Passmore, Ber. 1889, 22, 2728; Sorokin, J. pr. Chem. [ii.] 37, 318; Kiliani and Loeffler, Ber. 1904, 37, 1196; Kiliani, *ibid.* 1908, 41, 158, 469; Rimbach and Heiten, Annalen, 1908, 359, 317; Nef, *ibid.* 1910, 376, 1.

SACCHARINS *v.* CARBOHYDRATES.

SACCHARONE $C_6H_8O_6 \cdot H_2O$. A substance obtained by the action of nitric acid on saccharin.

SACRED BARK *v.* CASCARA SEGRADA.

SAFETY EXPLOSIVES *v.* EXPLOSIVES.

SAFFLORITE *v.* SMALTITE.

SAFFLOWER (*bastard saffron*). This dyestuff consists of the dried florets of *Carthamus tinctorius* (Linn.), an annual thistle-like plant belonging to the *Cynarocephalœ*. A native of Southern Asia, it has been cultivated in China, India, Persia, Egypt, also in central and southern Europe. When in full bloom the yellow florets are plucked, and either at once dried, so as to form an orange-coloured fibrous mass somewhat resembling saffron, or they are first kneaded with water, in order to remove a useless yellow colouring matter, and then pressed into the form of lens-shaped cakes and dried.

Safflower owes its value to an insoluble red colouring matter which occurs only in very small amount, about 0·5 p.c., whereas the soluble yellow colouring matter is said to be present to the extent of about 30 p.c.

The yellow colouring matter may be obtained by first precipitating a cold aqueous extract of safflower with lead acetate and acetic acid and then adding ammonia to the filtrate, *i.e.* precipitating with basic lead acetate. The yellow precipitate thus obtained is carefully decomposed with dilute sulphuric acid, and after removing the lead sulphate the filtrate is evaporated to dryness with exclusion of air. It is thus obtained as an amorphous substance, having acid properties, a bitter taste, and a peculiar odour. It is of a very unstable character, and on exposure to air seems to oxidise, becoming brown and somewhat insoluble in water. According to Schlieper, its composition is represented by the formula $C_{16}H_{20}O_{10}$; according to Malin, it is $C_{24}H_{30}O_{15}$. This product is apparently a glucoside or contains a substance of this character, for after digestion with boiling dilute sulphuric acid, the solution yields to ether a small quantity of a crystalline yellow colouring matter (private communication).

Carthamin or *carthamic acid* is the name given to the useful red colouring matter, which, although insoluble in water, is readily soluble in alkaline solutions. To obtain it, safflower is well washed with slightly acidified water to remove the yellow colouring matter, then it is steeped for some time in a cold dilute solution of sodium carbonate. If the alkaline solution be now acidified with acetic or tartaric acids the carthamin is precipitated in so finely divided a condition that it cannot be successfully collected. This difficulty is, however, obviated by making use of the fact that carthamin is readily attracted and removed from its acidified solution by cellulose. Hence bleached cotton is immersed and moved about in the alkaline solution, which is at the same time gradually acidified with tartaric or citric acid.

In this manner the carthamin is slowly precipitated and is at once attracted by the cotton, which thus becomes dyed red. After washing the dyed cotton with slightly acidified water, the colouring matter is dissolved off by means of a dilute solution of sodium carbonate, from which the carthamin is thrown down, on the addition of tartaric acid, as a bright-red precipitate, which is now in a purer and more granular form. Further purification is effected by dissolving the dried precipitate in alcohol and reprecipitating with water.

Preisser, the first to investigate carthamin (J. pr. Chem. 1844, [i.] 32, 142), described this substance as colourless needles, which, by air-oxidation in the presence of alkali, were converted into carthamein, the true colouring matter. Schlieper (Annalen, 1846, 58, 357), however, proved that Preisser's statements were incorrect, and he isolated carthamin in the form of green, iridescent, red crusts, or as a granular, greenish-red powder, to which he assigned the formula $C_{14}H_{14}O_7$. When digested with boiling alcohol, it was converted into a yellow compound having the composition $C_{14}H_{14}O_9$. According to Malin (Annalen, 1840, 36, 117), carthamin gives *p*-hydroxybenzoic acid when digested with boiling potassium hydroxide solution.

Radcliffe (J. Soc. Dyers, 1897, 13, 158), by extracting an air-dried commercial paste extract of safflower with methyl alcohol, subsequently evaporating the solution, and adding hot water, obtained a product crystallising in red, iridescent needles, melting at 168°–169° (provisional), which, when exposed to sunlight, changed to a red powder. A study of the absorption spectra of solutions of carthamin, and an account of its general properties, are described in his paper, but the author reserved analytical details for a later communication.

Kametaka and Perkin (Chem. Soc. Trans. 1910, 97, 1415) have prepared carthamin in a crystalline condition. The dried and finely-ground commercial extract of safflower is extracted on the water-bath with successive quantities of pyridine, and the combined extracts are evaporated to a small bulk under reduced pressure. Warm water is then added until a faint turbidity occurs, and on standing a semi-solid crystalline mass is obtained, which is collected and washed with water. To remove a wax the crystals are digested first with chloroform and then with ether, and the product is purified by repeated crystallisation from pyridine and water. When crystallised in this manner carthamin contains pyridine of crystallisation, which is best removed by drying the substance at 125° or 160°.

Carthamin consists of bright scarlet-coloured prismatic needles which melt and decompose at about 228°–230°, is very sparingly soluble in methyl and ethyl alcohol, and insoluble in ether. It dissolves in cold dilute alkali hydroxides, sodium carbonate, and ammonia with an orange colour, and is reprecipitated by acids unchanged. With sulphuric acid carthamin forms a dull red coloured solution, which after heating to 100°, gives with water a violet precipitate, possessing feeble mordant dyeing properties, and is soluble in alkalis with a green colouration. Carthamin is decomposed by heating with dilute mineral acids with formation of a dull brown precipitate. The formula of carthamin is, or closely approximates to, $C_{25}H_{24}O_{12}$, and the anhydrous substance is extremely hygroscopic and takes up two molecules of water of crystallisation.

Monopotassium carthamin $C_{25}H_{23}O_{12}K$ is formed when the finely powdered colouring matter suspended in boiling alcohol is treated with strong aqueous potassium acetate solution. It consists of green iridescent needles, and is decomposed by hot water with liberation of the free colouring matter.

Benzoyl carthamin $C_{25}H_{17}O_{12}(C_7H_5O)_7$ consists of a pale red amorphous powder which melts and decomposes at about 230°–235°, and an *acetyl*- derivative has been prepared, the analysis of which agrees fairly well with the formula $C_{25}H_{17}O_{12}(C_2H_3O)_7$.

On account of the extreme sensitiveness of carthamin to alkali (*see* later) it does not appear to be possible to obtain a pure methylation product of this colouring matter by ordinary methods, and the employment also of diazomethane has not given a successful result.

With nitric acid carthamin yields *picric acid*, and when fused with alkali p-*hydroxybenzoic* and acetic acids are formed. By the action of boiling potassium hydroxide solutions varying in strength from 50 to 1 p.c., a brownish-yellow coloured liquid was quickly produced, which on neutralisation gave a brown precipitate, not susceptible to crystallisation. The filtrate from this was found to contain p-*coumaric acid*, and p-*hydroxybenzaldehyde*. No third product soluble in ether could be obtained by this reaction.

When carthamin in 1 p.c. sodium carbonate solution is treated with hydrogen peroxide p-*coumaric acid* is produced, and the crude methylation product of the colouring matter similarly treated gives p-*methoxycinnamic acid*. By oxidation with chromic acid *anisic acid* and *anisic aldehyde* are obtained.

Kametaka and Perkin were unable to prepare the yellow compound which, according to Schlieper (*l.c.*) and Radcliffe (*l.c.*), is produced by boiling carthamin with alcohol, and consider that the pure substance does not give this reaction. By boiling the colouring matter with alcoholic aniline, however, a yellow crystalline substance *aniline xanthocarthaminate*

$$C_{25}H_{24}O_{12}\cdot C_6H_7N$$

is readily formed. It consists of needles decomposing at 276°–278°, sparingly soluble in alcohol. In a similar manner *β-naphthylamine xanthocarthaminate* $C_{25}H_{24}O_{12}\cdot C_{10}H_9N$, orange-coloured leaflets, decomposing at about 266°–268° can be prepared, and the corresponding ψ-cumidine-derivative, orange-coloured leaflets, decomposes at about 290°.

These compounds are probably the salts of an acid which is termed *xanthocarthaminic acid*; it appears to be isomeric with carthamin, and is probably closely related to it. It was observed that when the β-naphthylamine compound is dissolved in potassium hydroxide solution, the clear yellow liquid becomes cloudy with separation of β-naphthylamine. When this latter is removed, and the alkaline liquid is neutralised with hydrochloric acid, a curdy yellow precipitate slowly separates, and this on standing gradually becomes red coloured, a change which is probably due to the reproduction of carthamin. On account of the large amount of oxygen which carthamin contains it is considered possible that an aliphatic nucleus may be present in this colouring matter.

Previous to the discovery of safranine and of the eosins, safflower was frequently used for the production of brilliant pinks or reds, chiefly on cotton or silk. The mode of dyeing is practically the same as that already given in describing the process of obtaining carthamin. The safflower in bags is well washed with cold water, in order to remove the yellow colouring matter, and the red colouring matter is then extracted by a treatment with a cold dilute solution of sodium carbonate. In this solution the material to be dyed is worked about, at the same time adding 'lime juice' (citric acid) gradually until in slight excess. Safflower extract is applied in a similar manner.

Dyers usually give the washed safflower several successive treatments with alkali, employing at first weak and afterwards strong alkaline solutions. The weak solutions give the brightest and purest tints; hence very delicate colours were dyed with these alone, whilst full colours were first dyed with the inferior extracts, and then 'topped' or 'bloomed' by a dyeing in the purer solutions. The shades obtained from safflower were at one time considered to be the finest and most delicate which a dyer could produce. On the other hand, they were not only expensive but had the disadvantage of being extremely unstable.

Safflower is a very weak dyestuff, for 4 oz. are necessary to dye 1 lb. of cotton light pink, 8 oz. for a rose-pink, and about 1 lb. to produce a full crimson.

It is now rarely, if ever, employed in Europe as a dyestuff, but large quantities are still cultivated, more especially in India, and employed for dyeing and pigment manufacture in the East.

Carthamin was sold in a more or less pure condition as a thin aqueous paste, under the name of *Safflower extract* or *Safflower carmine*, but this product is now difficult to obtain in Europe. On the other hand, considerable quantities are still manufactured in Japan, where it is very largely employed as a cosmetic. Carthamin ground up with starch, talc, &c., is used as rouge.

For other references *v.* Dumas, Annalen, 27, 147; Liebermann, Ber. 7, 247; 8, 1649; Döbereiner, J. Phys. Chem. 26, 266; Salvetat, Ann. Chim. Phys. [3] 25, 337; J. pr. Chem. 44, 475; Dufour, Ann. Chim. Phys. 48, 283.

A. G. P.

SAFFLOWER OIL (*Saffron oil*). Safflower oil is obtained from the seeds of *Carthamus tinctorius* (Linn.), a plant until recently cultivated all over India for the preparation of the saffron dye. The chief localities where the plant is grown are Bengal, Hyderabad, Cawnpore, Bombay, and the Punjab. Two distinct varieties of the plant are grown, *Carthamus tinctorius* (Linn.), and *Carthamus Oxyacantha* (Bieb.). The cultivation of the plant has also been extended to Egypt, the Caucasus, and Turkestan. The seeds contain from 30 to 32 p.c. of oil, but owing to the thick husk, only 17 to 18 p.c. of the oil are obtainable by pressing. The press-cake contains, therefore, a large amount of woody fibre as the following analysis of a pressed cake shows:—

	Per cent.
Albuminoids . . .	20·11
Oil	11·91
Starch, sugar, &c. . .	10·83
Woody fibre . . .	40·75
Moisture	11·60
Ash	4·80

The ordinary Anglo-American rollers have been found unsuitable on account of the extreme hardness of the husk.

The oil is prepared in India on a small scale from two kinds of fruits—the cultivated white and glossy form, and the small fruit of a mottled brown, grey, or white appearance. The oil obtained from the cultivated variety by expression in the cold is pale yellow; it has a pleasant taste simulating that of sunflower oil, so that it can be used largely for edible purposes. Considerable quantities are pressed in India together with other seeds, especially arachis nuts.

The saturated fatty acids contained in safflower oil consist of palmitic and stearic acids, the unsaturated fatty acids consist of oleic and linolic acids, and small quantities of linolenic acid. (For the characteristics *see* OILS AND FATS.)

Safflower oil has good drying powers, and although it cannot replace linseed oil in all its applications, it should certainly form a substitute for it in many instances, and find extended use in the manufacture of soft soap.

Safflower oil is heated by the natives to obtain an oil suitable for the preservation of leather vessels, ropes, &c., exposed to the action of water. A specimen of oil thus prepared had the sp.gr. 0·9634, the saponification value 188·0, and the iodine value 128·9. It therefore represents a kind of 'boiled oil.' This 'boiled oil,' termed by the natives 'roghan,' is employed in Lahore, Delhi, Bombay, and Calcutta for the manufacture of 'Afridi wax linoleum.' It is also used by the natives for drawing artistic designs on woven cloth, the production of which was considered for a long time a valuable secret. The pattern is made by means of finely pointed staves dipped in the 'roghan,' which is drawn in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

Considerable quantities of safflower oil are used as a burning oil, notably in Egypt.

J. L.

SAFFRON consists of the dried petals of the *Crocus sativus* (Linn.), a plant which flowers in September and October, and is distinct from the ordinary spring crocus [*Crocus vernus* (All.)]. It is a native of the East, but is cultivated in Spain, the South of France, and Austria, and is employed for flavouring purposes, for the staining of articles of diet, and to a very limited extent as a dyestuff. Saffron contains the aromatic oil known as *saffron oil*, *picrocrocin*, a bitter compound, and *crocin* or *polychroit*, the glucoside of the colouring matter crocetin.

Crocin $C_{44}H_{70}O_{28}$ forms a yellowish-brown amorphous powder, readily soluble in water and dilute alcohol, and dissolves in sulphuric acid with a deep blue colouration which, on standing, becomes violet, then red, and finally brown.

When digested with hot dilute hydrochloric or sulphuric acids crocin is hydrolysed into crocetin and glucose, a reaction which, according to Kayser (Ber. 17, 2228), proceeds as follows:

$$2C_{44}H_{70}O_{28}+7H_2O=C_{34}H_{46}O_9+9C_6H_{12}O_6.$$

Crocetin consists of a red amorphous powder, readily soluble in alcohol and soluble in alkaline solutions with an orange-red colour. With lead acetate it gives a red precipitate, and with sulphuric acid a deep blue-coloured solution. Kayser assigned the formula $C_{34}H_{46}O_9$ to crocetin, but according to Wiess (J. pr. Chem. 101, 65) this is more probably $C_{16}H_{18}O_6$. Again, Schunck and Marchlewski (Annalen, 278, 357) find that Kayser's analytical figures are in agreement with a much simpler formula $C_{15}H_{20}O_4$.

Crocetin dyes aluminium and tin mordanted fabrics, respectively, dull orange and yellow shades.

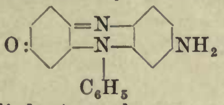
According to Rochleder, the Chinese dyestuff 'Wongsky' (*q.v.*), which consists of the fruit of the *Gardenia grandiflora* (Lour.), also contains crocin (J. 1858, 475). A. G. P.

SAFFRON OIL *v.* SAFFLOWER OIL.

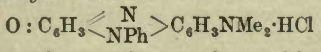
SAFFRON SURROGATE *v.* VICTORIA YELLOW.

SAFRANINES and *apo*-**SAFRANINES** *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM.

SAFRANINONES. *Safraninone*,



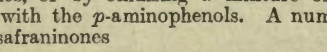
(*Aminobenzolindone*) may be prepared by oxidising a mixture of molecular proportion of *p*-phenylene diamine and *m*-hydroxy diphenylamine with potassium dichromate (Jaubert, Ber. 1895, 28, 270); by heating phenosafranine hydrochloride with aqueous sodium acetate at 150° (Fischer and Hepp, Ber. 1897, 30, 399); by heating safranol with ammonia at 180°, and in other ways (Jaubert, *l.c.*). It forms prisms with bluish-green lustre, readily soluble in water with a red colour and brownish-yellow fluorescence. When heated with ammonia at 180° it forms a little phenosafranine, and when boiled with alkalis it yields safranol and ammonia. Safraninone forms a blue diazo- compound, which condenses with β-naphthol giving a blue colouring matter. The *acetyl* derivative of safraninone forms fine, red needles, with copper-like lustre, and melting above 280°. Safraninone also condenses with aldehyde, and when heated with sulphur and alkali sulphides, it forms a violet cotton dye (D. R. P. 126175; Chem. Zentr. 1901, ii. 1108). The hydrochloride of the *dimethyl derivative*



$$O:C_6H_3{<}{\overset{N}{\underset{NPh}{}}}{>}C_6H_3NMe_2{\cdot}HCl$$

is a brownish crystalline powder, readily soluble in water (Joubert, *l.c.*).

Safraninones containing aliphatic groups are very readily prepared by the further oxidation of the indophenols obtained either by condensing the nitrosophenols with the 4-alkyltolylene-2:4-diamines, or by oxidising a mixture of these bases with the *p*-aminophenols. A number of these safraninones

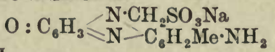


$$O:C_6H_3{<}{\overset{NR}{\underset{N}{}}}{>}C_6H_2Me{\cdot}NH_2HCl$$

have been described (D. R. P. 189078).

They form valuable substances for the preparation of red sulphur dyes.

The product of reaction of molecular proportions of an aldehyde bisulphite and *m*-tolylenediamine is mixed with an alkaline solution of nitrosophenol, and after making slightly acid and stirring for a few hours, the mixture is made slightly alkaline and oxidised with manganese dioxide. When formaldehyde bisulphite is used the safraninone

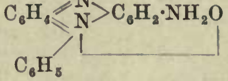


$$O:C_6H_3{<}{\overset{N{\cdot}CH_2SO_3Na}{\underset{N-C_6H_2Me{\cdot}NH_2}{}}}$$

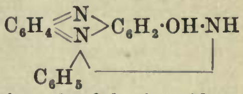
is formed.

Sulphide dyestuffs which dye cotton reddish shades are obtained by heating these safraninones with sodium sulphide and sulphur, with or without addition of metallic salts (Eng. Pat. 24008, 1906).

Iso-Safraninone



or



is obtained by the action of sulphuric acid on pheno-*iso*-safranine.

The violet-brown glistening needles of the *iso*-safraninone chloride obtained on adding sodium chloride is purified and its aqueous solution is treated with ammonia or ammonium carbonate when the *iso*-safraninone separates as blackish-brown needles, m.p. 310°–315° (decomp.) readily soluble in hot water and in alcohol with a green colour (Kehrmann and Kramer, Ber. 1900, 33, 3074).

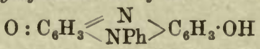
SAFRANISOL, SAFRANOLS *v.* AZINES.

SAFRANONE (*Benzolindone, Aposafranone*) $O:C_6H_3{<}{\overset{N-}{\underset{NPh}{}}}{>}C_6H_4$ is prepared by treating the ferric chloride double salt of phenylphenazonium chloride with excess of sodium hydroxide (Kehrmann and Schaposchnikoff, Ber. 1897, 30, 2623). It may also be obtained by treating anilinoaposafranine with barium hydroxide at 140° (Fischer and Hepp, Annalen, 1895, 287, 193), or aposafranine hydrochloride with sodium hydroxide (Kehrmann, Ber. 1895, 28, 1716); by removing the amino- group from safraninone or by heating azo-safranine with 75 p.c. sulphuric acid (Jaubert, Ber. 1895, 28, 275), and by other methods (Kehrmann and Burgin, *ibid.* 1896, 29, 1819).

Safranone forms small brown needles with a green metallic lustre, m.p. 248°–249°, and dissolves with a magenta colour in water, and with a green colour in sulphuric acid, which turns to rose colour on dilution.

When treated with phosphorus oxychloride it yields chlorophenylphenazonium chloride (Fischer and Hepp, Ber. 1897, 30, 1827; *ibid.* 1898, 31, 299). According to Fischer and Römer (*ibid.* 1907, 40, 3406) the amino- group may be introduced by means of hydroxylamine, only into such safranones as have both the ortho-position, with respect to the oxygen atom, free.

Hydroxysafranone or *safranol*



$$O:C_6H_3{<}{\overset{N}{\underset{NPh}{}}}{>}C_6H_3{\cdot}OH$$

may be prepared by heating an aqueous solution of nitrosophenol with *meta*-hydroxydiphenylamine and sodium hydroxide (Hewitt, Newman and Winmill, Chem. Soc. Trans. 1909, 580), or by oxidising a mixture of *p*-amino phenol and *meta*-hydroxyphenylamine in presence of mineral acid (Jaubert, *l.c.*), and by other methods (Fischer and Hepp, Ber. 1895, 28, 2283; *ibid.* 1896, 29, 361; *ibid.* 1905, 38, 3435). It is a crystalline substance, m.p. above 330°, almost insoluble in most ordinary solvents, but readily soluble in alkalis.

The *ethyl* (m.p. 265° decomp.) and *methyl* ethers (m.p. 240°) (Fischer and Hepp, Annalen, 1895, 286, 212), the *acetyl* (m.p. 271°) Hewitt, *l.c.*), the *sulphonic acid*, and *naphtho* derivatives (Jaubert, Ber. 1898, 31, 1185), have been prepared. When heated with sulphur and an alkali sulphide, safranol forms a bluish-violet cotton dye (D. R. P. 126175; Chem. Zentr. 1901, ii. 1107).

Halogen (Fischer and Hepp, Ber. 1900, 33, 1485) and other derivatives of safranone have been prepared (Kehrmann, *ibid.* 1895, 28, 1712; Fischer and Hepp, *ibid.* 2287; Kehrmann and Führer, Annalen, 1896, 290, 301; Kehrmann and Duret, Ber. 1898, 31, 2437; Fischer and Hepp, Chem. Zentr. 1902, ii. 903).

SAFROLE (*safrol, shikimole*) $C_{10}H_{10}O_2$ (St. Evre, Ann. Chim. Phys. [iii.] 12, 107; Grimaux and Knotte, Compt. rend. 68, 928) is contained in camphor oil, a waste product of camphor distillation, and gives to it its characteristic odour (Chemist & Druggist, 40, 592). Safrole is the essential constituent of oil of sassafras (from *Sassafras officinale* (Nees) [*Laurus Sassafras* (Linn.)]), of which it forms 78 p.c. (Power and Kleber, Pharm. Review, 1896); it also occurs in many other plants of the order *Lauraceae*, in the essential oil of *Illicium religiosum* (Sieb. et Zucc.) (Flückiger, J. Pharm. Chim. [iii.] 17, 989; Eijkman, Rec. trav. chim. 4, 32), in massoybark oil (Woy, Arch. Pharm. [iii.] 28, 22), and in oil of *Cinnamomum zeylanicum* (Nees) (Duyk, J. Pharm. d'Anvers, 1896, April; *see* also Goulding, Chem. Soc. Trans. 1903, 1099).

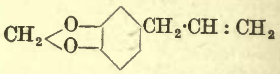
Safrole is obtained from 'red-oil' (a product of fractionating camphor oil, containing 20 p.c. of safrole), or from oil of sassafras, by freezing it out; and is purified by recrystallisation.

At ordinary temperatures it is a clear, colourless oil, having an odour of sassafras and a sharp taste. Cooled to −20° it solidifies in rhombic prisms (ratio of axes; $a:b:c = 0{\cdot}31658 : 1 : 0{\cdot}57832$, $\beta = 111°\ 59'{\cdot}5$, Arzruni, N. Rep. Pharm. 25, 615); m.p. 12° (Sugiyama, J. Soc. Chem. Ind. 1902, 1551), 8·5°–10° (Arzruni), 8° (Schiff, Ber. 17, 1935); b.p. 230°–235° (Sugiyama), 232° (Schiff); sp.gr. 1·107 at 15°; impure commercial safrole has sp.gr. 1·1040–1·1065 (Sugiyama).

Safrole is used in soaps to cover the odour of the fatty basis, and has been introduced into America, under the name of *safrine*, as an artificial oil of sassafras.

Safrole $CH_2O_2 : C_6H_3{\cdot}C_3H_5$ can exist in four isomeric forms, all of which are known; the commercial product is a mixture of two or more of these.

Safrole, the *methylene ether* of *allyldihydroxy benzene* (Poleck, Ber. 22, 2861), has the formula



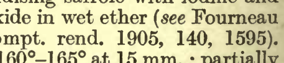
This is confirmed by the molecular refraction 78·11 and the molecular dispersion 7·14, which agree well with the calculated values (Brühl, Ber. 21, 457; Gladstone, Chem. Soc. Trans. 1891, 295); by its synthesis from magnesium methyl iodide and piperonal, *via* ethyl piperonyl alcohol (Mameli, Atti. R. Accad. Lincei. 1904, 13, ii. 315); and by its behaviour on oxidation with potassium permanganate, a 1½ p.c. solution of which at 70°–80° oxidises it to methylene-3 : 4-dihydroxybenzylglycol

$$CH_2O_2 : C_6H_3{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

crystallising from benzene in white needles, m.p. 82°–83°. With stronger solutions of $KMnO_4$ it gives piperonal, piperonic acid, and α-homopiperonic acid (Tiemann, Ber. 24, 2879; Poleck, *ibid.* 19, 1094; Ciamician and Silber, *ibid.* 23, 1159). Both safrole and *iso*-safrole are reduced by Sabatier and Senderen's method to *m*-propyl-phenol, but not quantitatively (Henrard, Chem. Weekblad, 1907, 4, 630).

When safrole is treated with an alcoholic solution of mercuric acetate a *mercuriacetate* $CH_2O_2 : C_6H_3{\cdot}C_3H_3(OH){\cdot}Hg{\cdot}OAc$ is formed which, with sodium chloride, gives the *mercurichloride* $CH_2O_2 : C_6H_3{\cdot}C_3H_3(OH){\cdot}HgCl$, a white crystalline powder, insoluble in water, decomposing at 170°, and reduced to safrole by Zn and NaOH (Balbiano and Paolini, Ber. 1903, 36, 3575). The action of mercuric acetate on safrole in presence of water gives a *glycol* $CH_2O_2{\cdot}C_6H_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3$; this when treated with zinc chloride gives an aldehyde $CH_2O_2{\cdot}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$ as a pale-yellow liquid, b.p. 145°–150° at 22 mm.; its *oxime* forms white laminæ, m.p. 158° (Balbiano and Paolini, Mem. R. Accad. Lincei, 1905, [v.] 5, 515).

Safrole is not acted upon by nitrosyl chloride, as is *iso*-safrole (Tilden and Forster, Chem. Soc. Trans. 1894, 334), and it does not form a picrate (Bruni and Tornani, Atti. R. Accad. Lincei, 1904, [v.] 13, ii. 184).



Safrole oxide $CH_2O_2 : C_6H_3{\cdot}CH_2{\cdot}\underbrace{CH{-\!\!-}CH_2}_{O}$ is prepared by oxidising safrole with iodine and yellow mercuric oxide in wet ether (*see* Fourneau and Tiffeneau, Compt. rend. 1905, 140, 1595). It is a liquid, b.p. 160°–165° at 15 mm.; partially decomposed on heating, yielding methylene dioxydihydrocinnamaldehyde (F. and T. *ibid.* 1905, 141, 662).

Bromo- derivatives of safrole; the following have been described by Woy (Arch. Pharm. [3] 28, 22):

$CH_2O_2 : C_6H_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$, liquid, b.p. 215°/22 mm.;

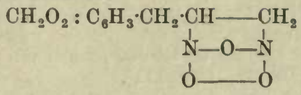
$CH_2O_2 : C_6H_2Br{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$, fibrous crystals, m.p. 54°;

$CH_2O_2 : C_6H_2Br{\cdot}CH_2{\cdot}CH : CH_2$, liquid, b.p. 185°–190°/18 mm.;

$CH_2O_2 : C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, small tabular crystals, m.p. 87°;

$CH_2O_2 : C_6HBr_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br.$

Safrole-α-nitrosite



$$CH_2O_2:C_6H_3{\cdot}CH_2{\cdot}\underset{\underset{O}{|}}{\underset{N}{|}}CH{-}\!\!{-}\underset{\underset{O}{|}}{\underset{N}{|}}CH_2 \quad (N{-}O{-}N)$$

is prepared by slowly adding dilute acid to KNO_2 solution covered with a solution of safrole in light petroleum (Angeli and Rimini, Gazz. chim. ital. 1895, 25, ii. 188). It is a yellow powder, m.p. 130°, with decomposition.

Safrole-β-nitrosite

$$CH_2O_2:C_6H_3{\cdot}CH_2{\cdot}CH(NO_2){\cdot}CH:NOH$$

is prepared by boiling the α-nitrosite with alcohol or alcoholic KOH. It is soluble in alkalis and has m.p. 92° (Angeli, Gazz. chim. ital. 23, ii. 101); converted by boiling dilute sulphuric acid into hydroxylamine and *nitropiperonylacetone* $CH_2O_2:C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}NO_2$ crystallising in colourless scales, m.p. 86°, from which, by boiling with $NH_2OH{\cdot}HCl$ and a little alkali, safrole-β-nitrosite is regenerated (Angeli and Rimini, Gazz. chim. ital. 1895, 25, ii. 188).

Dihydrosafrole $CH_2O_2:C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$, 3:4-methylenedioxy-1-propylbenzene, is prepared by the reduction of safrole or *iso*-safrole with sodium and alcohol. It is a colourless liquid, b.p. 228°, miscible with alcohol, ether, benzene, and acetic acid. It gives a methyl ether boiling at 212°–213° (corr.) (Ciamician and Silber, Ber. 23, 1159).

Nitrodihydrosafrole

$$CH_2O_2:C_6H_2(NO_2){\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

6-nitro-3:4-methylenedioxy-1-propylbenzene obtained by adding 45 p.c. HNO_3 to an acetic acid solution of dihydrosafrole, is a yellow crystalline solid, m.p. 36° (Thoms and Blitz, Arch. Pharm. 1904, 242, 85).

Aminodihydrosafrole, 6-amino-3:4-methylenedioxy-1-propylbenzene, is obtained by reducing the above compound with aluminium amalgam. It is an unstable substance, m.p. 24°, b.p. 156° at 11·5 mm.; its *hydrochloride* melts and decomposes above 200°; its *acetyl derivative* has m.p. 171·5°; its *benzoyl derivative* has m.p. 151°.

Dinitrodihydrosafrole

$$CH_2O_2:C_6H(NO_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3,$$

2:6-dinitro-3:4-methylenedioxy-1-propylbenzene, prepared by the action of fuming HNO_3 at 20° on nitrodihydrosafrole, is yellow, and melts at 121° (*v.* Thoms and Blitz, Arch. Pharm. 1904, 242, 85).

Diaminodihydrosafrole

$$CH_2O_2:C_6H(NH_2)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

is obtained by the action of aluminium amalgam on the preceding compound. It has m.p. 72°; the *monohydrochloride* has m.p. 246° with decomposition; *benzoyl derivative* melts at 248°.

Nitroaminodihydrosafrole ($NH_2:NO_2=2:6$), prepared by the action of ammonium sulphide on the dinitro-compound, melts at 76·5° (Thoms and Blitz).

***iso*-Safrole** (*isafrole*)

$$CH_2O_2:C_6H_3{\cdot}CH:CH{\cdot}CH_3$$

is the *methylene ether* of *propenyldihydroxybenzene* (Balbiano and Paolini, Ber. 1902, 35, 2994). It is obtained: (1) by heating safrole with alcoholic KOH (Ciamician and Silber, Ber. 23, 1159); (2) by heating safrole to 200° with dry NaOEt (Angeli, Gazz. chim. ital. 23, ii. 101); (3) by heating safrole with a solution of sodium amyloxide in amyl alcohol at 260° (Gassmann, Compt. rend. 124, 38).

That *iso*-safrole has the above constitution is shown (1) by its production on heating methylenebromocaffeic acid (Moureu, Compt. rend. 1896, 122, 792); (2) by its production from β-piperonyl-α-methyl acrylic acid by loss of CO_2 (Wallach, Annalen, 1907, 357, 72); (3) by its behaviour on oxidation. Mercuric acetate oxidises it to the *glycol*, $CH_2O_2:C_6H_3{\cdot}C_3H_5(OH)_2$, m.p. 101°–102° (Balbiano and Paolini, Ber. 1903, 36, 3575); it is oxidised by ozone to piperonal (Otto, Ann. Chim. Phys. 1898, [viii.] 13, 77).

iso-Safrole exists in two stereoisomeric forms which can be partially separated by fractional distillation:

α-iso*Safrole* is obtained by steam distillation of the first fractions, from which the safrole has been removed by mercuric acetate. The β-*iso*-safrole is fixed as the picrate and does not come over.

The α- compound has b.p. 116·2°–116·3° at 13·5 mm., 242·2°–242·5° at 760 mm., sp.gr. 1·1073 at 18·5°, n_D 1·5678 at 18°.

β-iso*Safrole* is the chief constituent of commercial *iso*-safrole and is most easily isolated as the picrate, m.p. 74° (*cf.* Bruni and Tornani, Atti. R. Accad. Lincei, 1904, [v.] 13, ii. 184). This, when decomposed by alcoholic NH_3, yields β-*iso*-safrole as an oil, b.p. 123° at 11·5 mm., sp.gr. 1·1227 at 21°/17·5°, n_D 1·5786 at 18°.

Both isomerides yield the same glycol and the same dibromide (Hoering and Baum, Ber. 1909, 42, 3076). By boiling *iso*-safrole with a mixture of PCl_3 and PCl_5 *di-iso-safrole* is obtained (Angeli and Mola, Chem. Soc. Abstr. 1895, i. 24).

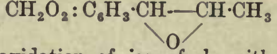
By heating *iso*-safrole hydrochloride with CH_3ONa, C_2H_5ONa, or C_3H_7ONa the following derivatives are obtained:—

Methoxy derivative. b.p. 110°–112° at 5 mm.; sp.gr. 1·1116 at 15°; n_D 1·51619 at 15°;

Ethoxy derivative, b.p. 110°–111° at 3·5 mm.; sp.gr. 1·0796 at 15°; n_D 1·50884 at 15°.

Amyloxy derivative, b.p. 136°–137° at 13·5 mm.; sp.gr. 1·0258 at 15°; n_D 1·49775 at 15° (Schimmel & Co. Chem. Soc. Abstr. 1905, i. 537). (For methods of distinguishing between safrole and *iso*-safrole, *see* Chapman, Analyst, 1900, 25, 313).

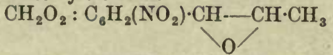
iso*Safrole oxide*



$$CH_2O_2:C_6H_3{\cdot}\underbrace{CH{-}\!\!{-}CH}_{O}{\cdot}CH_3$$

is formed by the oxidation of *iso*-safrole with iodine and mercuric oxide in alcohol (Bougault, Compt. rend. 1900, 130, 1766; Bull. Soc. chim. 1901, [iii.] 25, 444). It is a liquid, b.p. 140°–142° at 9 mm. (Hoering, Ber. 1905, 38, 2296); sp.gr. 1·2128 at 17° (Ber. 1905, 38, 3477; D. R. P. 174496).

Nitro-iso*safrole oxide*



$$CH_2O_2:C_6H_2(NO_2){\cdot}\underbrace{CH{-}\!\!{-}CH}_{O}{\cdot}CH_3$$

obtained by hydrolysis of β-bromonitro-α-acetoxydihydro-*iso*-safrole (*v. infra*), has m.p. 113°–114°.

Bromo-iso*safrole oxide*, b.p. 169°–173°, at 11 mm.; and

Dibromo-iso*safrole oxide*, m.p. 134°–135°, are prepared in an analogous manner.

When these oxides are distilled at the ordinary pressure or warmed with dilute acid they are converted into the isomeric *ketones*: $CH_2O_2 : C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, b.p. 283°–284°, sp.gr. 1·2017 at 17°; $CH_2O_2 : C_6H_2Br{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, m.p. 103°; $CH_2O_2 : C_6HBr_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, m.p. 116°–117° (Hoering, *l.c.*).

iso*Safrole dibromide*

$$CH_2O_2 : C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$$

is obtained by the action of bromine water on *iso*-safrole. Warmed with granulated marble in moist acetone it yields the *hydroxy bromide* $CH_2O_2 : C_6H_3{\cdot}CH(OH){\cdot}CHBr{\cdot}CH_3$, which with alcoholic KOH gives the *oxide* (Hoering, D. R. P. 174496).

Dibromo-iso*safrole dibromide*

$$CH_2O_2 : C_6HBr_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$$

is prepared by dropping *iso*-safrole quickly into bromine. It is reduced by zinc-dust to *dibromo*-iso*safrole*, crystallising in needles, m.p. 149°–150°.

Similarly *bromo*-iso*safrole*, m.p. 30°–33°, b.p. 165°–170° at 16 mm., can be obtained from *bromo*-iso*safrole dibromide.*

Tribromo-iso*safrole-aβ-dibromide* (*iso*-safrole pentabromide) $CH_2O_2 : C_6Br_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_3$ obtained by dropping *iso*safrole into excess of bromine, crystallises in clusters of colourless crystals, m.p. 196·5°–197°.

Tribromo-iso*safrole*

$$CH_2O_2 : C_6Br_3{\cdot}CH : CH{\cdot}CH_3$$

is produced by reducing the preceding compound with zinc-dust in alcohol; m.p. 110°–111°. Reduced with HI it yields *tribromodihydro*-iso*safrole.* Heated with alcoholic KOH at 145°–150° for 5–6 hours it gives the *ethoxymethyl ether* of *tribromopropylene catechol*

$$C_2H_5O{\cdot}CH_2{\cdot}O{\cdot}C_6Br_3(OH){\cdot}CH : CH{\cdot}CH_3,$$

m.p. 96°–99° (Hoering, Ber. 1907, 40, 1096).

β-Bromonitro-a-acetoxydihydro-iso*safrole* is obtained by the action of nitric acid on *iso*-safrole dibromide in alcoholic solution, in yellow prismatic needles, m.p. 113° (Hoering, Ber. 1905, 38, 3458). *β-Bromonitro-a-methoxydihydro*-iso*safrole* is similarly obtained as an oil, b.p. 166°–169° at 11 mm., and 158°–164° at 8 mm. (Hoering, *ibid.* 1905, 38, 3464).

Methoxydibromo-iso*safrole*

$$CH_2O_2 : C_6H_2Br{\cdot}CH(OMe){\cdot}CHBr{\cdot}CH_3$$

is produced by the action of MeOH on bromo-*iso*-safrole dibromide; forms needles or prisms, m.p. 75°–76°. The corresponding *ethyl compound* forms large rhombohedra, m.p. 58°–60° (Pond, Erb and Ford, J. Amer. Chem. Soc. 1902, 24, 327; *see* also Pond and Siegfried, *ibid.* 1903, 25, 262).

Dibromo-iso*safrole dichloride* $C_{10}H_8O_2Cl_2Br_2$, m.p. 97°–99°.

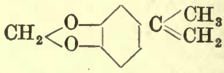
Tribromo-iso*safrole dichloride*

$$C_{10}H_7O_2Cl_2Br_3,$$

m.p. 173·5°–174·5° (Hoering and Baum, Ber. 1908, 41, 1914).

iso*Safrole nitrosite* $C_{10}H_{10}N_2O_5$, produced by the action of nitrous acid on iso*safrole*, forms colourless needles, m.p. 132° (Angeli, Ber. 24, 3994); m.p. 128° (Wallach, and Müller, Annalen, 1904, 332, 305). Warmed with acetyl chloride, sodium methoxide, or alcoholic KOH it yields *β-nitro*-iso*safrole* $CH_2O_2 : C_6H_3{\cdot}CH : C(NO_2){\cdot}CH_3$ in yellow needles, m.p. 98° (W. and M.; *cf.* Angeli and Rimini, Gazz. chim. ital. 1896, 26, i. 7). Treated with hydroxylamine, hydrochloric acid and sodium carbonate in alcohol it yields *piperonaldoxime*, m.p. 111°.

ψ-Safrole



(1-ψ-allyl-3: 4-catechol-methylene ether) is obtained by the action of magnesium methyl iodide on methyl piperonylate as a colourless liquid, sp.gr. 1·1338 at 0°; 1·1198 at 15°; b.p. 135° at 20 mm., 233°–239° at 760 mm.; n_D 1·5619 at 15°. On reduction it yields 1-iso*propyl*-3 : 4-*catechol-methylene ether,* and on oxidation *piperonyl acetone.* It forms an iodohydrin,

$$CH_2O_2 : C_6H_3{\cdot}C(CH_3)(OH){\cdot}CH_2I,$$

which, when treated with KOH, forms an *ethylene oxide,* b.p. 150°–155° at 15 mm. (Béhal and Tiffeneau, Bull. Soc. chim. 1908, [iv.] 3, 729).

ψ-Safrolechlorhydrin

$$CH_2O_2 : C_6H_3{\cdot}CMe(OH){\cdot}CH_2Cl,$$

prepared by the action of moist chlorine on ψ-safrole, is a yellow coloured oil. By treatment with PCl_5 and subsequent hydrolysis it is converted into *dihydroxyphenyl-ψ-allyl chlorohydrin* $C_6H_3(OH)_2{\cdot}CMe(OH){\cdot}CH_2Cl$, a thin oil from which *a-methyl adrenalin* is obtained as a bright golden-yellow powder (Böttcher, Ber. 1909, 42, 253).

SAFROSINE *v. Phthaleïns*, art. TRIPHENYLMETHANE COLOURING MATTERS.

SAGAPENUM *v.* GUM RESINS.

SAGE CAMPHOR *v.* CAMPHORS.

SAGE OIL *v.* OILS, ESSENTIAL.

SAGO. A product consisting mainly of starch, prepared from the pith of certain palms. *Metroxylon laeve* (Mart.), *M. Rumphii* (Mart.), and *Raphia pedunculata* (Beav.) or *Metroxylon Sagu* (Rottb.) yield the true sago, though the name is given to products derived from other palms, *e.g.* the Indian palm, *Caryota urens* (Linn.). Large quantities of sago are obtained from the Malacca and Philippine Islands and New Guinea. The sago palms grow best in boggy soils, rich in humus, and each tree yields about 600 lb. of starch (Dubose, Dingl. poly. J. 1892, 285, 213).

The palms are cut down when the trunks have attained a height of about 20 ft. and a diameter of 20 ins., and the sap allowed to drain away; they are sawn into lengths of 6–8 ft., split open, and the pith, consisting of starch granules intermixed with fibrous matter, removed. This is then pounded in wooden mortars and agitated with water. The milky liquid is then run through sieves to remove fibre and cellular matter and allowed to settle. The sediment is repeatedly washed with water, drained and dried. It constitutes sago flour, and is exported to Europe in that form, for the manufacture of glucose and for use in the textile industries.

A sample examined by Balland (J. Pharm. Chim. 1903, 17, 476) gave the following analytical figures—

Water	Protein	Fat	Starch	Crude fibre	Ash
12·1	2·1	0·2	80·4	4·0	1·2

Samples of sago flour, as imported into

England, were examined by Smetham (J. Roy. Lancashire Agric. Soc. 1909), who found—

	Water	Protein	Fat	Sol. carbohydrates	Crude fibre	Ash
Sago flour . .	16·8	0·25	0·23	82·3	0·13	0·59
„ „ (seconds)	16·3	1·12	0·17	76·9	3·30	3·80

Granulated sago or pearl sago—the form in which sago is chiefly used as a food—is prepared from sago flour by mixing it with water to form a stiff paste, which is forced through a metal sieve into a heated shallow metal dish which has been slightly greased. The fragments are kept stirred by means of an iron rod and agglutinate into small spherical masses which are usually sorted into sizes and sold in two or three forms, ‘ bullet sago,’ ‘ pearl sago,’ &c.

Singapore is the chief seat of the sago industry; in 1892 its production amounted to 20,000,000 kilos. (Dubose, *l.c.*).

Sago starch consists mainly of oval or rounded granules, some of which are compound, consisting of one large granule with 1, 2, or 3 smaller ones attached. The large granules are 50–60μ in length, the smallest ones 10–20μ. There is a distinct, lineal, transverse, or oblique hilum and distinct striations: often vegetable tissue, cells, and hairs, due to imperfect washing in preparation, are also present.

Pearl sago, under the microscope, shows starch granules in various stages of transformation, some retaining their original shape, others in which the starch has been more or less gelatinised, whilst some are swollen into irregular, shapeless masses.

When heated with water, pearl sago does not fall to pieces, but the spherical masses swell up and become gelatinous and almost transparent.

Pearl sago usually contains 12–15 p.c. of water and a small quantity (about 0·15 p.c.) of inorganic matter, the rest being almost all starch, with, doubtless, small quantities of dextrin.

Imitations of pearl sago, prepared from potato starch, have been produced in France and Germany, in some cases, colouration by oxide of iron being adopted (Wittstein, Dingl. poly. J. 1878, 227, 93). H. I.

SAINFOIN, *Onobrychis viciaefolia* (Scop.) [=*O. sativa* (Lam.)]. A deep-rooted, perennial, leguminous plant grown for pasturage and hay. It prefers light, calcareous soils, and should be cut early, as after flowering its stems become woody. It yields a vigorous after-growth.

The following analyses are from Kellner:—

	Water	Protein	Fat	N-free extract	Fibre	Ash	Digest. proteids
Beginning to flower	81·0	3·6	0·6	7·9	5·5	1·4	1·9
In full flower	80·0	3·5	0·6	7·8	6·9	1·2	1·6
Hay, cut before flowering	15·8	15·4	3·2	34·0	24·9	6·7	7·8
Hay, cut in flower	16·5	13·2	2·5	32·5	28·0	7·3	7·5

The ash, like that of other *Leguminosæ*, is rich in lime; according to Wolff's analyses, it contains—

K_2O	Na_2O	MgO	CaO	P_2O_5	SO_3	SiO_2	Cl
39·4	1·7	5·8	32·2	10·4	3·3	4·0	3·0

H. I.

SAJODIN *v.* Synthetic drugs.

SAKÉ. A very popular drink in Japan. It is prepared from rice by fermentation, the manufacture being carried on from September to February only, as in the summer the fermentation cannot be properly controlled. It is a light-yellow liquid, having a peculiar flavour somewhat resembling a mixture of beer and sherry. Its sp.gr. is about 0·99, and it contains on an average 17 p.c. of alcohol by volume, or nearly 30 p.c. of proof spirit.

The manufacture is described by M. Ikuta (Zeitsch. anal. Chem. 14, 439) as follows:—

1. *Preparation of koji.* The finest rice is boiled in an iron kettle with sufficient water to soften it; after cooling, it is brought into the koji chamber, the outside walls of which are covered with earth and the interior with straw, by which means the temperature of the interior is kept up.

The rice is here mixed with a little *moyaschi* (a yeast obtained from a previous fermentation) and remains in the chamber for two days, by which time most of the starch of the rice is converted into dextrose, and it is then called *koji.*

2. *Preparation of motoh. Koji,* fresh-boiled rice, and water are mixed in a wooden vat in the proportion to form a thin paste. Wooden casks containing warm water are placed in this liquid every day; after one or two days a frothy fermentation takes place, which is allowed to continue 30–40 days, during which time the temperature rises to 37°; at the end of the period the liquid contains 10 p.c. of alcohol, and is called *motoh.*

3. *The third stage.* Freshly boiled rice, *koji* and *motoh* are mixed with a little water. The mixture ferments a little, but without appreciable rise in temperature. As soon as the froth ceases to form on the surface, *i.e.* in 8–10 days, the process is finished. The fermented fluid is filtered through cotton bags and put into casks, and allowed to stand until clear. It is heated in an iron vessel to 44°, and is then run into casks.

The residue remaining in the cotton sacks has been used from time immemorial in Japan for the manufacture of vinegar.

The preparation of saké is accelerated, and a more uniform product obtained by steaming the rice, previously soaked in water, then spreading on mats and sprinkling with *Aspergillus oryzæ.* The mats are kept in the dark, and the mass, when covered with mould, is thoroughly mixed about twice every 24 hours for 3 or 4 days. The *koji* thus prepared is sometimes dried and preserved in this form for future use.

A fermented liquor is then prepared from a mixture of koji, water, and steamed rice, and this in its turn, is used for fermenting about seven times its weight of a mixture of boiled rice and water in nearly equal proportions, the whole process requiring about 30 days.

Saké is usually taken hot by the Japanese immediately before meals. It has intoxicating effects of a speedy but transient character.

A somewhat similar beverage is made from rice in Java and Borneo (*see* also Arrack).

J. C.

SAKURANIN *v.* Glucosides.

SAL ACETOSELLÆ. *Acid potassium oxalate v.* Oxalic acid.

SAL ALKALI MINERALE. *Sodium carbonate.*

SAL ALKALI VEGETABILE. *Potassium carbonate.*

SAL ALKALI VOLATILE SICCUM or **SAL VOLATILE.** *Ammonium sesquicarbonate.*

SAL AMARUM. *Magnesium sulphate.*

SAL AMMONIAC. *Ammonium chloride.*

SAL APERITIVUM FRIEDERICIANUM. *Sodium sulphate.*

SAL AURI PHILOSOPHICUM. *Acid potassium sulphate.*

SAL CATHARTICUM. *Magnesium sulphate.*

SAL CORNU CERVI. *Ammonium carbonate.*

SAL DE DUOBUS or **SAL DUPLICATUM.** *Normal potassium sulphate.*

SAL DIGESTIVUM SYLVII or **SAL FEBRIFUGUM SYLVII.** *Potassium chloride.*

SAL FUSIBILE. *Sodium ammonium phosphate.*

SAL MARINE. Common salt or *Sodium chloride.*

SAL MARTIS. Green vitriol or *Ferrous sulphate.*

SAL MICROCOSMICUM. *Sodium ammonium phosphate.*

SAL MIRABILE. *Sodium sulphate.*

SAL MIRABILE PERLATUM. *Disodium orthophosphate.*

SAL NARCOTICUM VITRIOLI. *Boric acid.*

SAL NATIVUM. *Sodium ammonium phosphate.*

SAL POLYCHRESTUM GLASERI, S. LAMERIANUM, S. PARISIENSE. *Normal potassium sulphate.*

SAL POLYCHRESTUM SEIGNETTI. *Rochelle salt ; Sodium potassium tartrate.*

SAL PRUNELLA. Fused nitre cast into sticks or balls.

SAL SATURNI. *Lead acetate.*

SAL SECRETUM GLAUBERI. *Ammonium sulphate.*

SAL SEDATIVUM HOMBERGII. *Boric acid.*

SAL SUCCINI. *Amber.*

SAL TARTARI. *Potassium carbonate.*

SALACETOL *v.* SALICYLIC ACID and SYNTHETIC DRUGS.

SALAERATUS. A term applied in the United States to a baking powder consisting of a mixture of sodium carbonate, salt, and cream of tartar or tartaric acid.

SALANTOL *v.* SALICYLIC ACID.

SALENIXON. Crude potassium sulphate, as obtained in the manufacture of nitric acid.

SALEP *v.* GUMS.

SALHYPNONE *v.* SALICYLIC ACID.

SALIBROMIN, SALIMENTHOL, and **SALIPYRIN** *v.* SYNTHETIC DRUGS.

SALICIN *v.* GLUCOSIDES.

SALICYLALDEHYDE (‘*salicylide*’)

$C_6H_4(OH)CHO$ (1, 2).

Occurs in the oil from *Spiræa Ulmaria* (Linn.) and other species of *Spiræa.* Obtained, along with the isomeric parahydroxybenzaldehyde, by the action of chloroform on an alkaline solution of phenol (Tiemann and Reimer, Ber. 1876, 824; Tiemann and Herzfeld, *ibid.* 1877, 63 and 213):

$$C_6H_5{\cdot}OH+CHCl_3+4NaOH = C_6H_4(ONa)CHO+3NaCl+3H_2O.$$

One part by weight of phenol, with 2 parts of caustic soda, is dissolved in at least 4 parts of water; the solution is heated to 50°–60° in a flask fitted with a reflux condenser, and 2 parts of chloroform are gradually added, shaking continually. The colour of the liquid changes from yellow to deep red. The reaction is completed by boiling the mixture for half an hour, after which the excess of chloroform is distilled off. The liquid is then acidified with sulphuric acid and steam-distilled, when salicylaldehyde passes over, along with unchanged phenol. The liquid remaining in the retort is filtered hot; on cooling, it deposits crystals of parahydroxybenzaldehyde. The salicylaldehyde is separated from the phenol by shaking an ethereal solution of the two substances with hydrogen sodium sulphite, with which the salicylaldehyde forms a crystalline compound; this is separated, and decomposed by treatment with sodium carbonate or dilute sulphuric acid, when the aldehyde is liberated.

Salicylaldehyde is also formed when salicin $C_{13}H_{18}O_7$ is oxidised with a mixture of potassium dichromate and dilute sulphuric acid (Schiff, Annalen, 150, 193); and by the reduction of salicylic acid with sodium amalgam, or electrolytically (H. Weil, Ber. 1908, 4147–4150).

Salicylaldehyde is manufactured by heating acetyl salicylic acid in an open vessel to 200°–210° for 5 or 6 hours. The product is cooled, and boiled with several successive quantities of water. The residue is dissolved in 4 or 5 times its weight of acetone and poured into 20–30 volumes of water, when the aldehyde is precipitated in cheese-like flakes, which are then dried (Wetter, Eng. Pat. 20188, 1902). Liquid, with a pleasant aromatic odour. Solidifies at −20° in large crystals, and boils at 196·5°; sp.gr. 1·1731 at 13·5°. Somewhat soluble in water, miscible in all proportions with alcohol or ether; the aqueous solution gives a strong violet colouration with ferric chloride. By reduction it yields saligenin $C_6H_4(OH)CH_2OH$; on oxidation, salicylic acid. When boiled with acetic anhydride and anhydrous sodium acetate it forms coumarin (*q.v.*). Forms salts with bases: thus $C_6H_4(OK)CHO$ and $C_6H_4(ONa)CHO$; the alkali salts are not decomposed by carbon dioxide. With sulphuryl chloride it yields *5-chlorsalicylaldehyde* (Peratoner, Gazz. chim. ital. 281, 235). Diiodosalicylaldehyde, mixed with a little monoidosalicylaldehyde, is obtained by treatment in dilute alcoholic solution with iodine and mercuric oxide (Seidel, J. pr. Chem. [ii.] 57, 205). By warming together salicylaldehyde, phenol, glacial acetic acid, and concentrated sulphuric acid, Liebermann (Ber. 9, 801; 11, 1436) obtained *hydroxy-aurin* $C_{19}H_{14}O_4$, a violet-red colouring matter. Zulkowsky found, among the products of the same reaction, an orange colouring matter which he termed *aurone*, assigning to it the formula $C_{26}H_{20}O_6$. Salicylaldehyde condenses with acetone and its derivatives in the presence of strong sulphuric acid, producing products which are converted on sulphonation into colouring matters which dye in shades from violet-red to blue-grey (D. R. P. 110520; Fabinyi, Chem. Zentr. 1900, ii. 301). If the condensation is effected in the presence of caustic soda di-*o*-oxydibenzalacetone results (D. R. P. 110521; Fabinyi, Chem. Zentr. 1900, ii. 302). E. Tummeley (Annalen, 251, 174–187) has produced a large number of azo- condensation products.

The isomeric *parahydroxybenzaldehyde* $C_6H_4(OH)CHO$ (1, 4), obtained as described in the foregoing, crystallises from water in needles melting at 115°–116°. The solution gives a very faint violet tinge with ferric chloride.

Metahydroxybenzaldehyde is produced by the reduction of *m*-hydroxybenzoic acid with sodium amalgam. It is prepared by reducing *m*-nitrobenzaldehyde with tin and hydrochloric acid, and adding potassium nitrite. On addition of concentrated hydrochloric acid the tin double salt crystallises out in white needles (Tiemann, Ber. 1882, 2045). It melts at 104° and boils at 240°. It gives only a faint violet colour with ferric chloride solution.

SALICYLIC ACID (o-*Hydroxybenzoic acid*) $C_6H_4(OH)COOH$. It occurs naturally in many plants as the methyl ester (*v. Esters, infra*), and is also found in small quantities in grapes, strawberries, and most fruits; hence it is found to a small extent in most wines (Portes and Desmoulières, J. Pharm. Chim. 1901, 14, 342; 1904, 19, 121; Ann. Chim. anal. 6, 401; Traphagen and Burke, J. Amer. Chem. Soc. 1902, 25, 242; Pellet, Ann. Chim. anal. 1907, 12, 10; 1910, 15, 302; Jablin-Gonnet, *ibid.* 1903, 8, 371; Süss, Chem. Zentr. 1903, ii. 841; Utz, *ibid.*; Griffiths, Chem. Soc. Proc. 1889, 122; Schneegans, J. Pharm. Chim. 1895, 2, 452; Windisch, Zeitsch. Nahr. Genussm. 1902, 5, 683). It is formed by the fusion of salicylaldehyde with potassium hydroxide (Piria, Annalen, 30, 165); and by the same process, from salicin (Gerhardt, *ibid.* 45, 21), coumarin (Delalande, *ibid.* 336), indigo (Cahours, *ibid.* 52, 343), *o*-cresol (Barthe, *ibid.* 154, 360), *o*-toluenesulphonic acid (Wolkow, Zeitsch. Chem. 1870, 326), and *m*-bromobenzoic acid (Hübner, Annalen, 162, 71). It is also formed by the action of nitrous acid on anthranilic acid (Gerland, *ibid.* 86, 47); by the electrolysis of a solution of benzoic acid in acetic acid (Bargellini and Inghilleri, Rend. Soc. Chim. di Roma, 1908, 6, 333), and by exposing solutions of benzoic acid to sunlight in the presence of a ferric salt (Nueberg, Biochem. Zeitsch. 1910, 27, 271).

Kolbe and Lautemann (Annalen, 115, 201) obtained it by passing carbon dioxide into a heated mixture of sodium and phenol. Kolbe afterwards found that dry sodium phenate, prepared from phenol and sodium hydroxide, could be substituted for the sodium and phenol in the foregoing reaction, and patented the following process, by which salicylic acid has been manufactured on a large scale (J. pr. Chem. 10, [ii.] 93; D. R. P. 426; Frdl. i. 229).

Crystallised phenol is dissolved in the equivalent quantity of concentrated sodium hydroxide and the solution is evaporated to dryness in shallow iron vessels, stirring thoroughly to prevent charring, and finally grinding it with a heavy pestle to a dry powder. The dry sodium phenate $C_6H_5\cdot ONa$, which is always of a reddish-yellow colour and very hygroscopic, is heated in a metal retort at first to 100°, and a current of dry heated carbon dioxide is passed in, constantly stirring the mass. The temperature is gradually raised, so that after a lapse of several hours it rises to 180°. After the heating has been continued for some time phenol begins to distil over, at first in small quantity, afterwards more abundantly. Finally the temperature is raised to 200°, and the operation, which lasts from 6 to 8 hours, is interrupted when no more phenol distils over at that temperature. It is necessary to keep up a rapid current of heated carbon dioxide in order that the liberated phenol may be removed as rapidly as possible from the retort, otherwise the mass cakes together, preventing further absorption. Half of the phenol originally present as phenate distils over during the process. The reaction takes place according to the equation

$$2C_6H_5\cdot ONa+CO_2=\underset{\text{Disodium salicylate (1, 2).}}{C_6H_4(ONa)COONa}+C_6H_5\cdot OH$$

The greyish-white mass of disodium salicylate remaining in the retort is, after cooling, dissolved in water and freed from resinous matters and coloured impurities by fractional precipitation with hydrochloric or sulphuric acid, after which the salicylic acid itself is precipitated by a further addition of the mineral acid.

The reaction which occurs was first explained by R. Schmitt (J. pr. Chem. [ii.] 31, 397), who showed that when carbon dioxide acts on sodium phenate in the cold, sodium phenyl carbonate is formed

$$C_6H_5\cdot ONa+CO_2=CO(ONa)(OC_6H_5).$$

When this compound is heated under ordinary pressures carbon dioxide is given off and only a small quantity of salicylic acid is formed, but when it is heated under pressure at 120°–140° it is converted quantitatively into the isomeric sodium salicylate

$$CO(ONa)(OC_6H_5)=C_6H_4(OH)COONa.$$

In this process the whole of the phenol is converted into salicylic acid, and it has the further advantage that, the temperature employed being lower, a purer product is at once obtained. For theory of reaction, *v.* Moll van Charante, Rec. trav. chim. 1908, 27, 58; Chem. Soc. Abstr. 1906, i. 665; Tijmstra, Ber. 1905, 38, 1375; de Bruyn and Tijmstra, Rec. trav. chim. 1904, 23, 385. Schmitt describes (D. R. P. 29939; Frdl. i. 233) three methods of carrying out the process: (1) The dry alkaline phenate (phenates of the alkaline earths may be substituted) is treated with carbon dioxide at ordinary temperature and pressure as long as absorption takes place, and the resulting compound is then heated in an autoclave for some hours at 120°–140°. (2) Carbon dioxide is pumped under pressure into an autoclave containing the alkaline phenate, cooling during the process, after which the autoclave is closed and left for some hours in order to allow the formation of the alkaline phenylcarbonate to be complete. It is then heated. (3) Instead of pumping in the carbon dioxide it is introduced in the form of solid carbon dioxide, and the autoclave is then quickly closed. The rest of the process is as in the preceding case (*v.* also J. Soc. Chem. Ind. 1885, 551). It has since been found, however (D. R. P. 38742; Eng. Pat. 7801; J. Soc. Chem. Ind. 1886, 501; Frdl. i. 234), that the process may be simplified by subjecting the alkaline phenate to the action of carbon dioxide under pressure at a temperature of 120°–140°, instead of at ordinary temperatures. These limits of temperature must not be exceeded, otherwise phenol is split off and the reaction takes place according to Kolbe's process. The alkaline phenyl-carbonate is converted, at the moment of its formation, into salicylate, thus completing the action in one stage instead of in two. Marasse (Eng. Pat. 17002; D. R. PP. 73279, 78708; J. Soc. Chem. Ind. 1893, 1055) heats an intimate mixture of phenol and potassium carbonate at 130°–160° and treats the product with the requisite quantity of carbon dioxide. Schering (D. R. P. 133500; Chem. Soc. Abstr. 1903, i. 343) substitutes the product obtained by the fusion of alkali benzene sulphonate and alkali hydroxide, for the sodium phenate in Kolbe's process. It is claimed that thus oxidation is hindered and alkali economised. Lederer (D. R. P. 80747; Frdl. iv. 151) heats the product obtained by condensing *o*-cresol and chloracetic acid with alkali at 260°–270°.

Salicylic acid is formed, together with *p*-hydroxybenzoic acid, the latter predominating, when an alkaline solution of phenol is boiled with carbon tetrachloride : $C_6H_5{\cdot}ONa+5NaOH+CCl_4 =C_6H_4(ONa)COONa+4NaCl+3H_2O$ (Reimer and Tiemann, Ber. 1876, 1285).

Salicylic acid is now prepared chiefly by the action of carbon dioxide on heated potassium phenate. There are three grades of acid on the market: (1) ordinary acid, the cheapest; (2) natural acid, the most expensive, but free from *p*-hydroxybenzoic acid, which is not entirely free from harmful physiological effects; (3) an intermediate acid, physiologically pure, and free from *p*-cresotic acid. The crude acid obtained by any of the above processes may be purified by neutralising a hot aqueous solution with calcium carbonate, allowing to cool and filtering off the calcium salt. This is then recrystallised from hot water until colourless, decomposed with hydrochloric acid, washed with cold water, and recrystallised from dilute spirit (Henderson, J. Soc. Chem. Ind. 1890, 591). For purification by means of stannous chloride or other tin salts *v.* Hofmann (D. R. PP. 65131, 67893; Frdl. iii. 826, 827). For special purposes, salicylic acid can be purified by fractional crystallisation of the silver salt with silver nitrate, any cresol derivative accumulating in the last fractions (Chemist and Druggist, 40, 590). The chief impurities in commercial salicylic acid are phenol, cresotic acid, *p*-hydroxybenzoic acid, and α-hydroxy*iso*phthalic acid. According to Henderson (*l.c.*) and B. Fischer (Pharm. Zeit. f. Russ. 1889, 28, 378; J. Pharm. Chim. 20, [5] 258) the presence of the two last-named compounds is due to unregulated temperature in the manufacturing process. Up to 150°, pure potassium salicylate is obtained, above 150° potassium *p*-hydroxybenzoate is also formed, and at 220° the latter compound is the main product. If alkali is present, *p*-hydroxybenzoic acid is produced. At a high temperature α-hydroxy*iso*phthalic acid is formed by the action of carbon dioxide on the potassium salicylate already formed. In a well regulated process, not more than 0·4 p.c. of these two acids is formed. To test for these impurities, 0·5 grm. of the acid is triturated in a mortar with 5 c.c. water and transferred to a test-tube. Two drops of a 2 p.c. solution of furfuraldehyde are added, and then 3 c.c. concentrated sulphuric acid without mixing. A brown ring shows the presence of *o*-cresotic acid, a faint violet ring that of *m*- or *p*-cresotic acids, and a blue ring above a yellow one indicates phenol (Carletti, Boll. chim. farm. 1907, 46, 421; Engelhardt and Jones, J. Soc. Chem. Ind. 1908, 1131). For other tests *v.* B. Fischer, *l.c.*; Ewell and Prescott, Analyst, 1888, 13, 237; Pharm. J. 19, [3] 380; Ferraro, Boll. chim. farm. 1908, 47, 789.

Properties.—Salicylic acid crystallises from hot water in slender needles and by spontaneous evaporation of its alcoholic solution, in monoclinic prisms (Marignac, J. 1885, 484). Very soluble in alcohol and ether, sparingly soluble in cold, readily in hot water (Walker and Wood, Chem. Soc. Trans. 1898, 620). For influence of sodium salts on the solubility, *v.* Philip, Chem. Soc. Trans. 1905, 987. M.p. 156·7° (corr.) (Fischer, *l.c.*; Dunstan and Blooch, Pharm. J. 1890, 21, [iii.] 429). Heat of combustion, &c., *v.* Berthelot and Recoura, Compt. rend. 104, 1571; Ann. Chim. Phys. 13, [6] 320; Stohmann, J. pr. Chem. 50, [2] 389; Delépine and Rivals, Compt. rend. 1899, 129, 520. When carefully heated salicylic acid sublimes without decomposition, but when quickly distilled breaks up into phenol and carbon dioxide (Graebe, Annalen, 139, 143). According to Graebe and Eichengrun (*ibid.* 1892, 269, 323) when heated at 195°–220° it splits up mainly into salol and xanthone. Chlorine reacts with salicylic acid to form mono- and di-substituted products (Tarugi, Gazz. chim. ital. 1900, 30, 487); for action of bromine (*v. Volumetric estimation*). Cold nitric acid reacts to form 5-nitrosalicylic acid, and fuming nitric acid to produce picric acid. By warming with phosphorus pentoxide, salicylmetaphosphoric acid is formed, which when heated with alcohols or phenols yields the esters of salicylic acid, but with 2 mols. of phenols at a higher temperature the dyestuff *salicyleine* is formed (Schultze, D. R. PP. 75830, 85565, 86319; Frdl. iv. 154, 155, 198). On reduction with sodium and amyl alcohol pimelic acid is the chief product (Einhorn and Willstäter, Ber. 1893, 2913; 1894, 331); reduction with sodium amalgam in the presence of boric acid yields salicylaldehyde (Weil, *ibid.* 1908, 41, 4147; Mettler, *ibid.* 4148). On standing for a long time solutions of salicylic acid develop a fungoid growth, which decomposes the acid; more rapidly on the addition of a little ferric chloride (Lott, J. Soc. Chem. Ind. 1903, 198).

Salicylic acid is extensively used as a food preservative. It is also used in medicine as an intestinal antiseptic, and in the treatment of gout and rheumatism. It has toxic properties and its salts cause albuminuria. It is excreted partly unchanged and partly as salicyluric acid (Bondznyski, Chem. Zentr. 1896, ii. 1039; *cf.* Jacoby, Biochem, Zeitsch. 1908, 9, 522, 527; Rockwood, J. Biol. Chem. 1909, 6). Salicylic acid dissolved in flexible collodion is used as a corn solvent.

Salicylic acid which is intended for use in medicine should be white and should show the proper melting-point. It should dissolve in cold concentrated sulphuric acid to form a colourless solution, and should leave no residue on ignition. Another method of testing the acid consists in dissolving the sample in absolute alcohol, allowing the solution to evaporate spontaneously and observing the points of the crystals formed: these will be colourless if the acid is pure, violet or pink if it contains iron, yellow or brown if resinous impurities are present.

Salicylic acid is used in the production of azo- dyes, such as *flavazol* and *chrysamin*. It influences the shade in the direction of yellow and tends to increase its fastness to light, though no dyestuff containing it is fast to chlorine (Bona, Farb. Zeit. 5, 120). *Azo- dyestuffs, v.* Gebek, Annalen, 251, 188; Kostanecki and Zibell, Ber. 1891, 1695; Landsteiner, Chem. Zentr. 1895, ii. 891; Paul, Zeitsch. angew. Chem. 1896, 679; Grandmougin, Guisan and Freimann, Ber. 1907, 40, 3450; Chem. Zentr. 1908, ii. 310; J. pr. Chem. 1908, 78, [ii.] 384; Nietzki, D. R. P. 44170; Frdl. ii. 323; Bayer & Co. D. R. PP. 61950, 31658; Ber. 1892; Ref. 530; Frdl. i. 465; Bad. Anil. u. Sod. Fabr. D. R. P. 58893; Ber. 1892, Ref. 928; Cassella & Co. D. R. P. 66351; Frdl. iii. 677; Leonhardt & Co. D. R. P. 38735; Frdl. i. 510. *Triphenylmethane dyestuffs, v.* Höchster Farb. D. R. P. 75803; Frdl. iv. 197.

It has also been recommended as a preservative in thiosulphate solutions (Bornträger, Zeitsch. anal. Chem. 27, 641).

Esters.

Methyl salicylate, *Oil of Wintergreen, Gaultheria oil,* $C_6H_4(OH)COOCH_3$. The chief natural sources of methyl salicylate are the leaves of *Gaultheria procumbens*, and the bark of the sweet birch (*Betula lenta*) (Power and Kleber, Pharm. Rundschau, 1895, 13, 228). In other plants it occurs chiefly as the glucoside, *Gaultherin*, which is hydrolysed to dextrose and methyl salicylate by the soluble ferment *betulase*. The following are the more important plants in which methyl salicylate is found: *Polygala Senega* (Linn.), *P. Baldwini* (Nutt.), *P. Variabilis* (H. B. & K.), *P. Javana* (DC.), *P. oleïfera* (Heck.), *P. serpyllacea* (Weihe), *P. calcarea* (Schultz), *P. vulgaris* (Linn.), *Gaultheria procumbens* (Linn.), *G. fragrantissima* (Wall.), *G. leucocarpa* (Blume.), *Betula lenta* (Linn.), *Spiræa Ulmaria* (Linn.), *Erythroxylum Coca* (Lam.), *Hypopitys multiflora* (Scop.), *Camellia Thea* (Link.), *Acacia caesia* (Wight and Arn.), *A. pluricapitata* (Steud.), *A. pennata* (Willd.). *A. Farnesiana* (Willd.) and *Viola tricolor* (Linn.). (Kremers and James, Pharm. Rev. 1898, 16, 100; Bourquelot, Compt. rend. 1894, 119, 802; J. Soc. Chem. Ind., 1899, 1153). It can be prepared synthetically by boiling a mixture of salicylic acid, sulphuric acid, and methyl alcohol under a reflux apparatus (Cahours, Ann. Chim. Phys. 10, [3] 327). Colourless oil, b.p. 222·2°, sp.gr. 4°/4° 1·1992, 15°/15° 1·189 (Perkin, Chem. Soc. Trans. 1896, 1238). For detection of free salicylic acid, *v.* Pharm. Centr. 1892, 33, 40; Zeitsch. anal. Chem. 32, 363. For estimation, *v.* Gibbs, J. Amer. Chem. Soc. 1908, 30, 1465.

Ethyl salicylate $C_6H_4(OH)COOC_2H_5$. Prepared by the action of ethyl alcohol and sulphuric or hydrochloric acids on salicylic acid (Cahours, Annalen, 52, 332; 74, 314; Göttig. Ber. 1876, 1473). B.p. 233·5°–234°; sp.gr. 4°/4° 1·1470; 15°/15° 1·372 (Perkin, *l.c.*). Physiological action, *v.* Houghton, Amer. J. Physiol. 1905, 13, 331.

Allyl salicylate, *v.* Akt. Ges. f. Anilfabr; J. Soc. Chem. Ind. 1910, 1332. Used medicinally and as a perfume.

Phenyl salicylate (*Salol*) $C_6H_4(OH)COOC_6H_5$. Prepared by the action of the chlorides or oxychlorides of phosphorus on a mixture of salicylic acid or a salicylate with phenol (Nencki, Eng. Pat. 8018; D. R. PP. 38973, 43713, 1622; J. Soc. Chem. Ind. 1886, 577; 1887, 561; Frdl. i. 237; ii. 314). Eckenroth (D. R. P. 39184; J. Soc. Chem. Ind. 1886, 677; Frdl. i. 240) has obtained it by the action of phosgene gas on a mixture of sodium salicylate and sodium phenate. Byk (Eng. Pat. 23449; J. Soc. Chem. Ind. 1894, 274) substitutes a mixture of phosphoric anhydride and phosphoric acid for phosphorus oxychloride. Emert (Eng. Pat. 14224; D. R. P. 62276; J. Soc. Chem. Ind. 1891, 1026; Frdl. iii. 835) heats salicylic acid at 220° in an atmosphere of carbon dioxide. Salol has also been prepared by the interaction of polysalicylide and phenol (Akt. Ges. f. Anilfabr. D. R. P. 73452; Frdl. iii. 835). The product obtained by these methods is usually steam distilled and finally purified by recrystallisation from dilute alcohol. Rhombic crystals, m.p. 43°; soluble in most organic solvents, but insoluble in water (Lusini, L'Orosi. 1903, 26, 89). When taken internally, it passes unaltered through the stomach, but is hydrolysed in the duodenum by the pancreatic ferment into phenol and salicylic acid (J. Soc. Chem. Ind. 1886, 577; *v.* also Humnicki, Chem. Zentr. 1899, i. 369; Bull. Acad. Sci. Cracow, 1908, 841; Lusini, L'Orosi. 1903, 26, 47). To avoid this resolution into phenol, *p-aminophenylacetyl salicylate* has been introduced into commerce under the name of *salophen* (van Eck, Chem. Weekblad. 1907, 4, 539; Cohn, J. pr. Chem. 61, [2] 550; Bayer & Co. D. R. PP. 62533, 60289; Frdl. iii. 836). This is hydrolysed into salicylic acid and *p*-aminophenol, an innocuous product which is eliminated without further change. *Salolchlorocarbonate, v.* F. Bayer & Co. D. R. PP. 109933, 114025, 118537; Chem. Soc. Abstr. 1901, ii. 697. For estimation of salol, *v.* Squire and Caines, Pharm. J. 1905, [iv.] 20, 720; in surgical dressings, Telle, J. Pharm. Chim. 1901, 13, 49; 14, 289; in mouth washes, &c., Beythien and Athenstadt, Zeitsch. Nahr. Genussm. 1907, 14, 392. *Phenylacetylsalicylate, Acetyl salol, Vesipyrin* (Knebel, J. pr. Chem. 1891, 43, 378; Zernik, Apoth. Zeit. 1907, 22, 152) is a white tasteless powder, m.p. 97°. The name *salol* is now often used to mean the compounds formed by the condensation of a substituted phenol with a substituted hydroxy- acid. *Halogenated salols, v.* Eckenroth and Wolf, Ber. 1893, 3463; Kauschke, J. pr. Chem. 1895, 51, [2] 210; Kolbe, Eng. Pat. 6749; J. Soc. Chem. Ind. 1894, 275). *Cresalols* are the compounds formed by condensation of the cresols with salicylic acid (Kolbe, Eng. Pats. 13169, 17221; J. Soc. Chem. Ind. 1889, 817; 1892, 58). α- and *β-Naphthyl salicylates, Salinaphthols,* known respectively as *Alphol* and *Betol,* are prepared in a similar manner (Byk, *l.c.*). Betol is used as an intestinal antiseptic in ague and articular rheumatism. For distinction of alphol from betol, *v.* Dragendorff, Arch. Pharm. 1895, 233, 612.

Benzyl salicylate, *v.* Akt. Ges. f. Anilfabr. D. R. PP. 119463, 144002; Chem. Soc. Abstr. 1901, i. 712; Chem. Zentr. 1903, ii. 1040.

SALTS.

The monobasic salicylates of the formula $C_6H_4(OH)COOR$ are mostly soluble in water, the dibasic salicylates $C_6H_4(OR)COOR$ being mostly insoluble (Piria, J. 1885, 485; Milone, Gazz. chim. ital. 15, 219).

Sodium salicylate $NaC_7H_5O_3,H_2O$ crystallises in colourless plates, very soluble in water and alcohol (Massol, Ann. Chim. Phys. [7] 1, 217; de Coninck, Bull. Acad. roy. Belg. 1907, 651). Also known anhydrous (Chemist and Druggist, 40, 590), and with $6H_2O$ (Romyn, Ned. Tydschr. Pharm. 1896, 111). Heated in air to 300° it decomposes into the disodium salt, carbon dioxide and phenol, but in an atmosphere of carbon dioxide 4-hydroxy*iso*phthalic acid $C_8H_6O_5$, and hydroxytrimesic acid $C_9H_6O_7$ are formed. Taken internally, sodium salicylate causes increased katabolism of proteid material (Goodbody, J. Physiol. 1900, 25, 399; Baldoni, Arch. exp. Path. Pharm. Suppl. 1908, 54). For assay of sodium salt, *v.* Alcock, Pharm. J. 1906, 23, 597. For double salt with sodium lactate, *v.* Tollner, D. R. P. 84378; Frdl. iv. 1188.

Potassium salicylate $KC_7H_5O_3,\frac{1}{2}HO$. When heated to 200° it changes into the dibasic salt of *p*-hydroxybenzoic acid, carbon dioxide, and phenol (Ost, J. pr. Chem. [2] 11, 329).

Lithium salicylate $LiC_7H_5O_3$. White crystalline powder, soluble in water and alcohol. Heated to 300°, it is transformed into the dibasic salt, no para- compound being produced. Used in cases of chronic or acute rheumatism.

Ammonium salicylate $NH_4C_7H_5O_3$, *v.* Sabanjew, J. Russ. Phys. Chem. Soc. 31, 380; Marignac, J. 1855, 485.

Salicylates of the alkaline earths, *v.* Milone, *l.c.*; Tarugi and Checchi, Gazz. chim. ital. 1901, 31, ii. 417.

Ferric salicylate $Fe(C_7H_5O_3)_3$. Formed as a brown precipitate on mixing ferric chloride and salicylic acid; quickly acquires a violet colour. For theory of reaction, *v.* Rosenthaler, Arch. Pharm. 1904, 242, 563; Hopfgartner, Monatsh. 1908, 28, 689; Desmoulières, J. Pharm. Chim. 1902, [vi.] 16, 241.

Aluminium salicylate $Al_2(C_7H_5O_3)_6,3H_2O$. Prepared by adding a solution of an aluminium salt to that of sodium salicylate. Used as a dusting powder in catarrhal affections of the nose and pharynx under the name of *Salumen* (Allen's Commercial Organic Analysis, 1910, iii. 488).

Aluminium ammonium salicylate

$$Al_2[C_6H_4(ONH_4)CO_2]_6,2H_2O.$$

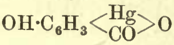
A neutral soluble salt more stable in solution than in the dry state. Used as an astringent wash for the throat and nose under the name of *Soluble Salumen* (Heyden Nachf., D. R. P. 81819; Frdl. iv. 1190; Allen, *l.c.*).

Aluminium potassium salicylate

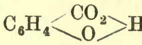
$$Al_2[C_6H_4(OK)CO_2]_6.$$

Used as a combined antiseptic and astringent under the name of *Alkasal* or *Alkasol* (Athenstädt, D. R. P. 78903; Frdl. iv. 1189; Allen, *l.c.*).

Mercuric salicylate $Hg(C_7H_5O_3)_2$. Prepared by adding a solution of mercuric acetate to one of sodium salicylate acidified with acetic acid (Buroni, Gazz. chim. ital. 1902, 32, ii. 311). On boiling the solution there is formed the anhydride of *hydroxymercurisalicylic acid*



$$OH{\cdot}C_6H_3{<}{Hg \atop CO}{>}O$$

(Buroni, *ibid.* 305; Lintner, Zeitsch. angew. Chem. 1900, 707). According to Lajoux (J. Pharm. Chim. 1907, 17, 412) the latter has the constitution  $C_6H_4{<}{CO_2 \atop O}{>}Hg$, and it may be prepared by gradually adding freshly precipitated yellow mercuric oxide to a boiling solution of salicylic acid (Lajoux and Grandval, J. Pharm. Chim. v. 20, 5; Compt. rend. 117, 44).

Bismuth salicylate. The basic bismuth salicylate of commerce, which is extensively used in medicine, is more correctly *bismuthyl salicylate* $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}BiO,H_2O$. According to Martinotti and Cornelio (Boll. chim. farm. 1901, 40, 141) it probably also contains the compound $C_6H_4(OH)COOBi(OH)_2$ (*v.* also Causse, Compt. rend. 113, 547). It may be prepared by saturating 40 c.c. of concentrated hydrochloric acid with bismuth oxide in the presence of 500 c.c. of saturated sodium chloride solution; to another 500 c.c. of brine 9 grms. of sodium hydroxide and 22 grms. of sodium salicylate are added. The two solutions are mixed, and the precipitate washed with water containing a few drops of nitric acid (Causse, *l.c.*). Microscopical prisms (*v.* also Fischer and Grützner, Arch. Pharm. 231, 680). Causse (Compt. rend. 112, 1220) has described a bismuth salicylate having the constitution $Bi(C_7H_5O_3)_3,4H_2O$. Thibault (Ann. Chim. Phys. 1902, [vii.] 25, 268; J. Pharm. Chim. 1901, 14, 32; Bull. Soc. chim. 1901, iii. 25, 794) has prepared a bismuth salicylate having the constitution $Bi_2O_3(C_7H_6O_3)$. Bismuth disalicylate $OH{\cdot}Bi(O{\cdot}CO{\cdot}C_6H_4{\cdot}OH)_2$ or

$$O[Bi(O{\cdot}CO{\cdot}C_6H_4{\cdot}OH)_2]_2$$

is prepared by adding crystalline bismuth nitrate to an aqueous solution of sodium salicylate, and after thorough mixing, the free acid is extracted with an indifferent solvent (Chem. Farb. *v.* Heyden, Eng. Pat. 19375; D. R. P. 168408; Chem. Soc. Abstr. 1906, i. 665).

Estimation of bismuth salicylate, *v.* Lyon, Pharm. J. 1904, iv. 18, 219; Harrison, *ibid.* 1908, 81, 349; Kollo, Proc. Amer. Pharm. Assoc. 1899, 719.

Bismuth cerium salicylate. An insoluble pink powder used in the treatment of diseases of the gastric and intestinal mucous membranes (Allen, iii. 491).

Cerous salicylate $Ce_2(C_7H_5O_3)_6,3H_2O$ (*v.* Morgan and Cahen, Pharm. J. 1908, 78, 428).

Cadmium salicylate $Cd(C_7H_5O_3)_2$. Prepared by treating salicylic acid with cadmium oxide or carbonate. Lustrous crystals; possesses valuable antiseptic properties (Caesaris, L'Orosi, 17, 262).

Copper salicylate, *v.* Ley and Erler (Zeitsch. anorg. Chem. 1908, 56, 401).

Salicylates of the rare earths, *v.* Zimmer & Co. (Eng. Pat. 13459; J. Soc. Chem. Ind. 1896, 606).

DERIVATIVES.

Sodium theobromine-salicylate

$$C_7H_7N_4O_2Na+C_6H_4(OH)CO_2Na.$$

Known as *Diuretin*. Prepared by mixing aqueous solutions of molecular proportions of sodium theobromine and sodium salicylate, and evaporating to dryness. Used as a diuretic in cases of scarlet fever, nephritis, &c. (J. Soc. Chem. Ind. 1890, 544). *Barutine* (Brat, Chem. Zentr. 1905, ii. 1189; Akt. ges. f. Anilf. D. R. P. 167140; Chem. Soc. Abstr. 1906, i. 692) is the corresponding barium compound and *Uropherin* the lithium compound.

Bornyl salicylate $C_{15}H_7O{\cdot}CO{\cdot}C_6H_4OH$. Known as *Salit.* Prepared by heating a mixture of French oil of turpentine and salicylic acid has b.p. 171°–173°/5 mm. (Tardy, J. Pharm. Chim. 1904, 20, [ii.] 57; Farb. v. Heyden., D. R. P. 175097; Chem. Soc. Abstr. 1907, i. 429).

Quinine salicylate $C_{20}H_{24}N_2O_2,C_7H_6O_3,H_2O$. White needles, used as an antipyretic in typhus and as a remedy for rheumatism and gout. Soluble in 225 parts of cold water, and 20 parts of 90 p.c. alcohol.

Salicyl derivatives of the Cinchona alakaolids, *v.* F. Bayer & Co. D. R. P. 137207; Chem. Soc. Abstr. 1903, i. 513.

Antipyrine salicylate $C_{11}H_{12}N_2O,C_7H_6O_3$ (*Salipyrin*). Crystalline odourless powder, having a pleasant taste and possessing the properties of its constituents, m.p. 91° *circa.* (Patein and Dufau, Bull. Soc. chim. 15, [3] 847; Schuyten, Chem. Zentr. 1899, ii. 38; 1901, ii. 484; Bourgeois, Rec. trav. chim. 18, 451). For estimation, *v.* Altschul, Pharm. Centr. Halle. 1893, 33, 61.

Tolypyrine salicylate, Tolysal, m.p. 91°. Resembles salipyrin. **Colchecine salicylate, Colchisal,** is used in the treatment of arthritis, rheumatism, and gout: yellow amorphous powder, soluble in water, alcohol, and ether. A mixture of colchicine and methyl salicylate is also called *colchisal.* **Saloquinone,** the quinine ester of salicylic acid $C_6H_4(OH)CO_2C_{20}H_{23}N_2O$, is used as an analgesic. **Rheumatine,** the salicylate of saloquinone, is used in the treatment of rheumatism. **Phenolphthalein disalicylate,** *v.* Knoll & Co. D. R. P. 212892; Chem. Soc. Abstr. 1909, i. 932. **Brucine salicylate,** *v.* Hilditch, Chem. Soc. Trans. 1908, 1391. **Hydroxyethyl salicylate,** *v.* Bad. Anil. u. Sod. Fab. D. R. P. 173776; Chem. Soc. Abstr. 1906, i. 957. **Alkyloxyalkyl esters,** *v.* F. Bayer & Co. D. R. P. 146849; Chem. Soc. Abstr. 1905, i. 318. **Acylsalicylic acids,** *v.* Lassar Cohn and Löwenstein, Ber. 1908, 41, 3360; Einhorn, Rothlauf, and Seuffert, *ibid.*, 1911, 44, 3309; Farb. v. F. Bayer, D. R. PP. 201325, 201326, Chem. Soc. Abstr. 1908, i. 984. **Alkyl- and aryloxyacylsalicylic acids,** *v.* Farb. v. Heyden, D. R. P. 221385; J. Soc. Chem. Ind. 1910, 650. **Carboxyalkylsalicylic acids,** *v.* Einhorn, Eng. Pat. 24009; J. Soc. Chem. Ind. 1910, 649. **Alkyloxymethyl ethers,** *v.* Farbenfab v. Elberfeld Co., U.S. Pat. 706018; J. Soc. Chem. Ind. 1902, 1154. **Alkyloxyalkylidene esters,** *v.* U.S. Pat. 740628; J. Soc. Chem. Ind. 1903, 1306. **Alkylaminoalkyl esters,** *v.* Meister, Lucius and Bruning, D. R. P. 188571; J. Soc. Chem. Ind. 1908, 644. **Benzoylmethylsalicylate, Salhpynone,** prepared from sodium salicylate and bromacetophenone, m.p. 113°–114° (Pharm. Centr. H. 37, 103). **Piperidine salicylate,** *v.* Hewitt, Eng. Pat. 19823; J. Soc. Chem. Ind. 1899, 855. **Glyceryl ester,** *v.* Sorger, Eng. Pat. 3367; U. S. Pat. 882590; Fr. Pat. 373854; J. Soc. Chem. Ind. 1907, 778. **Menthol ether,** *v.* Bibus and Scheubler, Eng. Pat. 8544; U. S. Pat. 830043; J. Soc. Chem. Ind. 1906, 233. **Cinnamylsalicylic acid,** *v.* Wellcome, Jowett and Pyman, Eng. Pat. 7125; Chem. Soc. Proc. 1907, 317; J. Soc. Chem. Ind. 1906, 1002. The **Dithiosalicylic acids** are used as substitutes for iodoform. Their sodium salts, known as *Dithion*, are antiseptics, and are used in the treatment of rheumatic fever and of foot and mouth disease (Cassella & Co., D. R. P. 189200; Chem. Soc. Abstr. 1908, i. 177; Farb. v. Heyden, Eng. Pats. 13027, 14443, 5263; D. R. PP. 51710; 64347; Frdl. ii. 141; iii. 840; J. Soc. Chem. Ind. 1890, 213, 821; 1892, 369; Baum, D. R. PP. 46413, 71425; Frdl. ii. 140; iii. 841). The basic bismuth salt, under the name of *Thioform*, is used to treat diseases of the eye, ear, and nose, and in veterinary surgery as a substitute for iodoform in eczema, erysipelas, &c. Of the halogenated salicylic acids, the iodo acids find application in medicine. 2-5-**Diodosalicylic acid** (Lautemann, Annalen, 120, 304) is used as an analgesic, antithermic, and antiseptic compound. The methyl ester, *Sanoform*, is used as a desiccant for wounds and ulcers and as a substitute for iodoform. *Monoiodo acids*, *v.* Hasse, D. R. P. 224536; Chem. Soc. Abstr. 1910, i. 740.

Salicylsulphonic acid $C_6H_3OH(SO_3H)COOH$ (Remsen, Annalen, 179, 107), also known as *sulphosalicylic acid*, is used in the treatment of articular rheumatism. It is also a delicate reagent for albumin and a precipitant for all kinds of proteids in urine (Roch, Pharm. Centr. 1889, 30, 549). The sodium salt is used as a substitute for salol. By successive nitration and bromination of this acid, the colouring matters known as *salicylic orange* and *salicylic yellow* are obtained. The former is said to dye wool and silk dark yellow or orange, the latter yellow (Chem. Fab. auf Actien vorm. E. Schering, D. R. PP. 15117, of 1880; 15889 of 1881).

5-Nitrosalicylic acid $C_6H_3(OH)(NO_2)COOH$. Prepared by nitrating salicylic acid with a mixture of sulphuric and nitric acids; m.p. 230°. **5-Aminosalicylic acid** $C_6H_3(OH)(NH_2)COOH$. Prepared by the reduction of the above nitro-compound (D. R. P. 77806; Frdl. iv. 54; Fischer and Schaar-Rosenberg, Ber. 1899, 82). Used in the treatment of articular rheumatism and in the production of azo dyestuffs (Bayer & Co., D. R. P.P. 51504, 58271, 60494, 60500, 62133, 62134, 75293, 86314; Frdl. ii. 325; iii. 610, 612, 614 *et seq.*, 632; iv. 795; Kalle & Co., D. R. P. 11640; Chem. Zentr. 1901, i. 152); oxazine dyestuffs (Bad. Anil. u. Sod. Farb. D. R. P. 78710; Frdl. iv. 484); and sulphurised dyestuffs (Höchster, Farbw., D. R. P. 118440, 118702).

Acetylsalicylic acid $C_6H_4(OCOCH_3)COOH$ (*Aspirin*). Prepared by treating salicylic acid or sodium salicylate with acetyl chloride (Kraut, Annalen, 150, 11; Erdmann, Ber. 1899, 3572; *v.* also F. Bayer & Co., Eng. Pats. 27088, 9123; J. Soc. Chem. Ind. 1899, 1154; 1900, 373). Used instead of the salicylates, as being insoluble in the gastric juice, it is devoid of irritating effects on the stomach. **Salicyloacetic acid**, *v.* Meister, Lucius and Bruning, Eng. Pat. 12179; J. Soc. Chem. Ind. 1898, 487. **Acetamidoethylsalicylic acid** $C_6H_3(OC_2H_5)(NH{\cdot}COCH_3)COOH$ (*Benzacetin*) *v.* Kuchler and Buff, D. R. P.

71258; Frdl. iii. 88. Used in the treatment of neuralgia.

Acetonyl salicylate $C_6H_4(OH)CO_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (*Salacetol* or *Salantol*) (van Eck, *l.c.*; Fritsch, D. R. P. 70054; Frdl. iii. 839; Eng. Pat. 3961; J. Soc. Chem. Ind. 1894, 274) is used as a substitute for salol in the treatment of rheumatism, neuralgia, and influenza. For estimation, *v.* Eckenroth and Koch, Pharm. Zeit. 1893, 38, 593; Helbing and Passmore, *ibid.* 621. **Monoglycol ester** $C_6H_4(OH)CO{\cdot}O{\cdot}CH_2{\cdot}CH_2OH$ (*Spirosal*) (Bayer and Co., Eng. Pat. 4055; J. Soc. Chem. Ind. 1905, 1030; Impens, Pfluger's Archiv. 1907, 120, 1). Used in the treatment of rheumatism.

Phenyl and **naphthyl ethers** $RO{\cdot}C_6H_4{\cdot}COOH$ (*v.* Akt. Ges. f. Anifabr., Fr. Pat. 347734; J. Soc. Chem. Ind. 1905, 346) **Methyl and ethyl salicylglycollates** (*v.* Soc. Chem. Ind. Basle, Eng. Pat. 24672; J. Soc. Chem. Ind. 1905, 902). **Indoform** is the trade name given to a mixture of salicylic acid, acetylsalicylic acid, and methyl salicylate (Frericho, Apoth. Zeit. 1908, 23, 641). The condensation product of **gallic** and **salicylic acids** $OH{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}CO{\cdot}C_6H_2(OH)_3$, known as *Salitannol*, is used as an antiseptic and a substitute for salol (F. Bayer & Co., Eng. Pat. 9898; J. Soc. Chem. Ind. 1898, 487). The condensation product of **boric** and **salicylic acids**

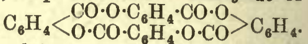
$$B{\cdot}OH(O{\cdot}C_6H_4{\cdot}COOH)_2,$$

Borosalicylic acid, and its sodium salt, known as *Borsalyl* or *Borosalyl*, are used as antiseptics. A mixture of hydrogen peroxide, boric acid, and salicylic acid, known as *Aseptin*, is used for the same purpose. Condensation product with *epi*- and *dichlorhydrins* (*v.* Lange, D. R. P. 184382; Chem. Soc. Abstr. 1907, i. 930). **Saliconitrile** $C_6H_4(OH)CN$. Prepared by treating salicaldoxime with acetic anhydride and subsequent hydrolysis (Tiemann, Ber. 1887, 3083; Spilker, *ibid.* 1889, 2771; Bone, Chem. Soc. Trans. 1893, 1350); m.p. 98°. Polymeride of saliconitrile (*v.* Miller, Ber. 1889, 2790).

Salicylamide $C_6H_4(OH)CONH_2$. Prepared by treating methyl or ethyl salicylates with concentrated aqueous ammonia at 100° (Spilker, Ber. 1889, 2767; Limpricht, Annalen, 98, 258; McCoy, Amer. Chem. J. 21, 116); m.p. 139·9° (corr.) (Remsen and Reid, *ibid.* 413); used in medicine as a substitute for salicylates. Labile isomerism among the benzoyl derivatives of salicylamide (*v.* Titherley and Hicks, Chem. Soc. Trans. 1905, 1207; Titherley, Chem. Soc. Proc. 1905, 288; McConnan and Titherley, Chem. Soc. Trans. 1905, 1314; Auwers, Ber. 1905, 38, 3256; 1907, 40, 3506; Einhorn and Schupp, *ibid.* 1905, 38, 2792; Einhorn and Haas, *ibid.* 3627).

Anhydrides of salicylic acid, **Salicylosalicylic acid** $O[C_6H_4{\cdot}COOH]_2$. Prepared by condensing salicylic acid or its salts with phosphorus trichloride or oxychloride, thionyl chloride, &c. (Gerhardt, Annalen, 87, 159; Märker, *ibid.* 124, 249; Kraut, *ibid.* 150, 13; Boehringer and Sons, Eng. Pat. 11457; U.S. Pat. 922995; D. R. PP. 211403, 214044, 220491; J. Soc. Chem. Ind. 1909, 382, 1104; 1910, 649), m.p. 47°–148°. Soluble without decomposition in sodium carbonate solution, but decomposed by boiling alkali hydroxide into salicylic acid; does not give a colouration with ferric chloride (Schiff, Annalen, 163, 219).

Disalicylide $(C_6H_4CO_2)_2$. Prepared by passing carbonyl chloride into an ice-cold solution of salicylic acid in pyridine (Einhorn and Pfeiffer, Ber. 1901, 34, 2951); m.p. 200°–201°. **Salicylide** or **Tetrasalicylide**



$$C_6H_4{<}\begin{matrix}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O\\O{\cdot}CO{\cdot}C_6H_4{\cdot}O{\cdot}CO\end{matrix}{>}C_6H_4.$$

Prepared by dissolving salicylic acid in toluene or xylene and gradually adding phosphorus oxychloride (Anschütz, Ber. 1892, 25, 3506; D. R. PP. 68960, 69708; Frdl. iii. 822, 824); m.p. 261°–262°. There is also formed a polymeride, m.p. 325°, from which it is separated by boiling with chloroform, a compound

$$(C_7H_4O_2)_4,2CHCl_3$$

being formed. Anschütz (Annalen, 1893, 273, 94) makes use of this in the preparation of pure chloroform. **Salicyl-α-methyl-phenyl-hydrazone**

$$C_6H_5(CH_3)N{\cdot}NH{\cdot}CH(C_6H_4)OH$$

is used in the treatment of neuralgia and rheumatism under the name of *Agathin* and *Cosmin* (Allen, *l.c.*).

DETECTION AND ESTIMATION.

A dilute aqueous solution of salicylic acid gives an intense violet colouration with ferric chloride. Free acids, especially hydrochloric and acetic acids, interfere with this reaction. Phenol and resorcinol also give a violet colour with ferric chloride, but the addition of two drops of lactic acid changes the colour to yellow-green in the case of phenol and resorcinol, whilst the colour produced by salicylic acid remains unchanged (Itallie, Apoth. Zeit. 4, 99). If phenols are present, Freyer (Chem. Zeit. 17, 69) recommends extraction with ether, evaporation to dryness and dissolution of the residue in absolute alcohol. If a violet colouration is produced with ferric chloride, salicylic acid is present as phenols give no colouration in alcoholic solution. A solution of copper sulphate, when added to a solution of salicylic acid or its salts, gives an emerald-green colouration in 2000 parts of water, destroyed by ammonia or acids. Solutions of silver nitrate or lead acetate give white precipitates with neutral salts, but not with the free acid. According to Endemann (J. Soc. Chem. Ind. 1896, 791), if salicylic acid is dissolved in formaldehyde solution, a red solid is precipitated in a magenta-coloured solution. A good test is that known as Millon's reaction (Lintner, Zeitsch. angew. Chem. 1900, 707). The solution is boiled with a few drops of a 10 p.c. solution of acid mercuric nitrate for 2 minutes; 2–3 drops of dilute sulphuric acid are added and then a few drops of a solution of sodium nitrite. A red colour is at once formed in the presence of salicylic acid. Jorissen recommends treating a solution of the acid or its salts with sodium nitrite and a little acetic acid, followed by 2 drops of copper sulphate solution: a blood-red colour is produced on boiling. For other tests, *v.* Reichard, Pharm. Zentr. H. 1910, 51, 743.

In the absence of any other acid substance, salicylic acid may be estimated by titration with standard alkali, using phenolphthalein as an indicator (Barthe, Bull. Soc. chim. 1894, 11–12, 516).

Volumetric methods. A known weight of the substance is dissolved in water to which a little sodium hydroxide has been added, and a volume containing about 0·1 grm. salicylic acid is diluted with water to 100 c.c. in a stoppered bottle. 10 c.c. hydrochloric acid, sp.gr. 1·1, are added and then a known volume of a solution of sodium bromide and sodium bromate, about 50–60 c.c., so as to give about 75 p.c. excess of bromine. In another bottle is placed an equal quantity of bromate solution. A 10 p.c. solution of potassium iodide is added to each bottle, and the liberated iodine titrated with N/10 thiosulphate solution. The difference in the volume of thiosulphate solution used in the titrations gives the amount of bromine which has reacted with the salicylic acid (Freyer, Chem. Zeit. 1896, 20, 820; Fresenius and Grünhut, Zeitsch. anal. Chem. 1898, 38, 292; von Generisch, Zeitsch. Nahr. Genussm. 1908, 16, 209; *cf.* Siedell, J. Amer. Chem. Soc. 1909, 31, 1168; Authenrieth and Beuttel, Arch. Pharm. 1910, 248, 112; Schulz, Bied. Zentr. 1907, 36, 602). Another method consists in precipitating salicylic acid from an alkaline solution with standard iodine solution and titrating back the excess of iodine with thiosulphate (Messinger and Vortmann, Ber. 1890, 23, 2753). Fresenius and Grünhut (*l.c.*) state that this method is inaccurate, but Messinger (J. pr. Chem. 1900, [iii.] 61, 236) and Bougault (Compt. rend. 1908, 146, 403) have shown that under proper conditions it is quite satisfactory.

Gravimetric method. When iodine is added to a solution of salicylic acid, a red precipitate is formed which consists of a mixture of the potassium salt of 3 : 5-diiodosalicylic acid and diphenylene quinone (Lautemann, Annalen, 1861, 120, 309; Benzinger and Kamerer, Ber. 1878, 11, 557). Bougault (*l.c.*) has devised a method for estimating salicylic acid, which depends on the insolubility of the latter compound. A portion of the substance containing about 0·1 grm. salicylic acid is weighed out and dissolved in a solution containing 1 grm. sodium carbonate in 50 c.c. water. Iodine is added, the solution heated for 20 mins. on the water-bath, and then boiled for 10 mins. under the reflux, iodine being added from time to time to insure excess being present. The excess of iodine is removed with sodium sulphite, the precipitate collected on a Gooch crucible, dried and weighed. This weight, multiplied by 138/344, gives the amount of salicylic acid present. For estimation as picric acid, *v.* Spica, Gazz. chim. ital. 1895, 25, i. 207; Montanari, *ibid.* 1904, 34, i. 207.

Colorimetric method (*v. Estimation in wines*).

Detection and estimation in wines. The methods differ chiefly in the solvent used to extract the salicylic acid. Ether was used at first, but it was found that it extracted another substance which coloured ferric chloride solution violet; probably the maltol of Brandt (Pereira, Bull. Soc. chim. 1901, [iii.] 25, 475; Wiegert, Chem. Zentr. 1888, 1511; Medicus, *ibid.* 1890, ii, 28; Spica, Gazz. chim. ital. 1895, 25, i. 207). The following solvents have been recommended: ether and light petroleum (Abraham, J. Pharm. Chim. 1898, [vi.] 8, 410; da Silva, Compt. rend. 131, 423; Ann. Chim. anal. 6, 11; Bull. Soc. chim. 1901, [iii.] 25, 726; Conrady, Apoth. Zeit. 1900, 15, 412; Pellet, Bull. de l'Assoc. Chim. Sucr. 1900, 18, 305; Ann. Chim. anal. 5, 418; 6, 364; Saporetti, Boll. chim. farm. 1908, 47, 751); chloroform (Weigert, *l.c.*; von der Heide and Jakob, Zeitsch. Nahr. Genussm. 1910, 19, 137); carbon tetrachloride (Bigelow, J. Soc. Chem. Ind. 1909, 1158); benzene (Lindeman and Motteu, Bull. Soc. chim. [iii.] 8, 441); and toluene (Bigelow, *l.c.*; Vitali, Boll. chim. farm. 1910, 45, 701; Cattini, *ibid.* 641). Harvey (Analyst, 1903, 28, 2) recommends the use of a 1 p.c. solution of iron alum, and proceeds as follows: 100 c.c. of wine are made acid with dilute sulphuric acid, and the salicylic acid extracted twice with ether. The ethereal solution is shaken out twice with water containing a known amount of N/2 or N/10 alkali. The solution is neutralised and made up to 250 c.c. 50 c.c. are taken and the intensity of colour obtained on the addition of ferric chloride compared with that in standard tubes containing a known amount of salicylic acid (*cf.* Pellet and de Grobert, Bull. de l'Assoc. Sucr. Dist. 1902, 20, 289; Cassal, Chem. News, 1910, 101, 289). *In beer.* Pinette (Chem. Zeit. 14, 1570; J. Soc. Chem. Ind. 1891, 165), Abraham (*l.c.*), Elion (Rec. trav. chim. 7, 211), Horn (*ibid.* 341), and Snyders (Chem. Zentr. 1888, 1186) use the ferric chloride method, whilst Schoepp (7th ed. Tydschr. Pharm. 7, 67; La Biere, 4, 182) prefers Millon's reagent (*v. supra*). *In milk* (Saporetti, *l.c.*; Revis and Payne, Analyst, 1907, 32, 286; Süss, Pharm. Centr. 41, 437; Breustedt, Arch. Pharm. 1899, 237, 170). *In foods.* 50 grms. of the crushed substance are placed in a 300 c.c. flask, a little water added, then 15–20 c.c. of a saturated solution of basic lead acetate, followed by 25 c.c. of sodium hydroxide to render the solution alkaline. 15–20 c.c. of N/1 hydrochloric acid are added and the mixture made up to 300 c.c. The hydrochloric acid dissolves the lead salicylate, leaving the lead tannate insoluble. Then colorimetrically with ferric chloride (Harry and Mummery, Analyst, 1905, 30, 124; von Fellenberg, Zeitsch. Nahr. Genussm. 1910, 20, 63; *cf.* Gorni, Rec. intern. Falsif, 1906, 19, 16; Boll. chim. farm. 44, 409; Dubois, J. Amer. Chem. Soc. 1906, 36, 602; Sherman, J. Ind. Eng. Chem. 1910, 2, 24; Taffe, Bull. Soc. chim. 1902, [iii.] 27, 701; Ann. Chim. anal. 1902, 7, 18; 1903, 8, 24; McElroy, J. Amer. Chem. Soc. 1894, 16, 198). *In urine*, *v.* Petermann, Ann. Chim. anal. 1901, 6, 4.

ISOMERIDES OF SALICYLIC ACID.

***m*-Hydroxybenzoic acid** $C_6H_4(OH)COOH$. Prepared by the action of nitrous acid on *m*-aminobenzoic acid (Gerland, Annalen, 91, 189), and by fusing *m*-benzenesulphonic acid (Barth, *ibid.* 148, 33; Graebe, *ibid.* 280, 67), *m*-chlorobenzoic acid (Remsen, Zeitsch. Chem. 1871, 81, 199; Dembey, Annalen, 148, 222), *m*-cresol (Barth, *ibid.* 154, 361), or benzoic acid (Barth and Schreder, Monatsh. 3, 802) with sodium hydroxide. Crystallises in microscopical laminæ, m.p. 188° (Kellas, Zeitsch. physikal. Chem. 24, 221), 200° (Fischer, Annalen, 127, 48). Gives no coloration with ferric chloride. Can be distilled unchanged; reduction with sodium amalgam yields *m*-hydroxybenzylalcohol. By heating with 90 p.c. sulphuric acid at 210°, *m*-benzdihydroxyanthraquinone, anthraflavic acid, and anthrarufin are produced; with sulphuric acid in the presence of boric acid, hexahydroxyanthraquinone is the product (Bayer & Co., D. R. P. 81959; Frdl. iv. 273).

p-**Hydroxybenzoic acid** $C_6H_4(OH)COOH$. Occurs in the pods of *Catalpa bignonioides* (Walt.). Prepared by the action of nitrous acid on *p*-aminobenzoic acid (G. Fischer, Annalen, 127, 145), and by fusing various gums (*e.g.* benzoin, dragon's blood) (Barth and Hlasiwetz, *ibid.* 134, 274; 139, 78), carthamin (Malin, *ibid.* 136, 117), tyrosin (Barth, *ibid.* 136, 112), phloretic acid (Barth, *ibid.* 152, 96), *p*-cresol (Barth, *ibid.* 154, 359), *p*-benzenesulphonic acid (Remsen, *ibid.* 178, 281), or benzoic acid (Barth, *ibid.* 164, 141; Barth and Schreder, Monatsh. 3, 802) with potassium hydroxide. It can also be prepared by heating potassium salicylate under pressure at 180° (*v.* Heyden Nachf, D. R. P. 48356, Frdl. ii. 132); by heating potassium phenate and carbon dioxide at 220° (*v.* Kolbe's process, *supra*); together with salicylic acid by boiling an alkaline solution of phenol with carbon tetrachloride (Reimer and Tiemann, Ber. 1876, 1285; *v. supra*); and as the ethyl ester by the hydrolysis of apigenin diethyl ether (Perkin, Chem. Soc. Trans. 1897, 815). Monoclinic prisms containing 1 mol. of water of crystallisation, m.p., 213°–214°, with decomposition (Negri, Gazz. chim. ital. 26, i. 65). For solubility, *v.* Walker and Wood, Chem. Soc. Trans. 1898, 622. Gives a yellow amorphous precipitate with ferric chloride. Distillation of the calcium salt yields phenol, salicylic acid, hydroxy*iso*phthalic acid, and carbon dioxide (Goldschmiedt and Herzog, Monatsh. 3, 132).

The only derivatives of medicinal importance are the following: Methyl *p*-amino-*m*-hydroxybenzoate, *Orthoform,* used as an antiseptic and local anæsthetic; the sodium salt of methyl-*p*-amino-*m*-hydroxybenzene sulphonate, *sulphonated orthoform,* and methyl-*m*-amino-*p*-hydroxybenzoate, *Orthoform new,* both of which are used as substitutes for orthoform (Einhorn, D. R. PP. 97334, 97335; Annalen, 311, 26; Ber. 1897, 991). They cannot be used for subcutaneous injections as they have an acid reaction. The glycocoll derivatives, however, are found to have a neutral reaction and have been used as anæsthetics (Einhorn and Oppenheimer, Annalen, 311, 154; D. R. P. 106502).

SALIFORMIN *v.* Synthetic drugs.

SALINAPHTHOL *v.* Salicylic acid.

SALINIGRIN *v.* Glucosides.

SALIT *v.* Salicylic acid and Synthetic drugs.

SALITANNOL *v.* Salicylic acid.

SALMON OIL. This oil is obtained on a very large scale from the salmon (*Salmo salar,* Linn.), as a by-product in the salmon preserving industry of British Columbia. The fish contains about 20 p.c. of oil. The oil is pale golden-yellow, has a mild smell, and a tolerably pleasant taste. For the characteristics, *see* Oils, Fixed, and Fats.

The oil is imported in large quantities into this country, and is used in the leather and soap industries. J. L.

SALMON RED *v.* Primuline and its derivatives.

SALOCHININ, SALOCOLL, SALOCRESOL, SALOPHEN, *v.* Synthetic drugs.

SALOL *v.* Salicylic acid.

SALOL-CHLORAL. An oily liquid

$$C_6H_4COOC_6H_5,O\cdot CH(OH)CCl_3,$$

obtained by heating salol with chloral hydrate.

SALSEPARIN *v.* Sarsaparilla.

SALT, COMMON, *v. Sodium chloride,* art. Sodium.

SALT, EPSOM. *Crystallised magnesium sulphate.*

SALT, FUSIBLE. *Sodium ammonium phosphate.*

SALT, GLAUBER'S. *Sodium sulphate.*

SALT, GLAZIER'S. *Potassium sulphate.*

SALT, MICROCOSMIC. *Sodium ammonium phosphate.*

SALT OF AMBER. *Succinic acid.*

SALT OF LEMERY. *Potassium sulphate.*

SALT OF LEMONS *v.* Oxalic acid.

SALT OF SATURN. *Lead acetate.*

SALT OF SODA. *Sodium carbonate.*

SALT OF SORREL *v.* Oxalic acid.

SALT OF TARTAR. *Potassium carbonate.*

SALT OF TIN. *Stannous chloride.*

SALT OF VITRIOL. *Zinc sulphate.*

SALT PERLATE. *Sodium phosphate.*

SALTPETRE. *Nitre; potassium nitrate.*

SALT, SEDATIVE. *Boric acid.*

SALUMIN *v.* Salicylic acid and Synthetic drugs.

SALVARSAN *v.* Synthetic drugs.

SALVIOL *v.* Camphors.

SALZBURG VITRIOL *v.* Copper sulphate.

SAMARIUM. Sym. Sa. At.wt. 150·4. In 1879 Lecoq de Boisbaudran isolated from samarskite the oxide *samaria* (*v.* Cerium earths, and Compt. rend. 88, 322; 89, 212), which was subsequently recognised by Brauner as occurring in the 'didymium' earth of cerite (Chem. Soc. Trans. 1883, 43, 278). The oxide obtained from samarskite by Delafontaine, to the metallic constituent of which the name '*decipium*' was given, consists partly of samaria (Compt. rend. 1878, 87, 632; *cf.* Marignac, *ibid.* 1880, 90, 899).

Occurrence. — Samarskite, cerite, orthite, ytterbite, monazite.

Separation and purification. Samarium was first separated by the fractionation of its double potassium sulphate, the solubility of which in aqueous alkali sulphate is greater than that of the neodymium and praseodymium double sulphates, but less than that of the corresponding salts of the terbium metals. The separation from the neodymium and praseodymium fraction can be effected by fractional precipitation with ammonia and from the terbium metals by crystallisation of the double sulphates (Cleve, Compt. rend. 1883, 97, 84; Bull. Soc. chim. 1885, [ii.] 43, 53). The neodymium and praseodymium can also be partially removed by fractional decomposition of the nitrates and the separation completed by crystallisation of the double sulphates (Bettendorf, Annalen, 1891, 263, 164). In these operations samaria shows itself to be a weaker base than neodymia or praseodymia, the element, samarium, occupying in the rare earth series a position between neodymium and the terbium metals as indicated by the solubilities of its salts and the basic strength of its oxide.

The most soluble portions of the double nitrate fractionations for neodymium and praseodymium, according to the methods of von Welsbach, Demarçay and Drossbach, may, therefore, be taken as a convenient starting material for the separation of samarium, and the double magnesium nitrate crystallisation in nitric acid (sp.gr. 1·3) affords a means of separating completely samarium from neodymium, the latter element having the less soluble double salt (Demarçay, Compt. rend. 1896, 122, 728). The more soluble double nitrates of europium and gadolinium are also eliminated by a prolonged application of this method (Compt. rend. 1900, 130, 1019, 1185; *cf.* Muthmann and Weiss, Annalen, 1904, 331, 1). A combination of crystallisation methods with simple nitrates and double magnesium nitrates has been employed in the separation of samarium and neodymium (Feit and Przibylla, Zeitsch. anorg. Chem. 1905, 43, 203).

The purification of the samarium double salt is facilitated by the addition of magnesium bismuth nitrate, which in the subsequent fractionation effects a separation between the double salts of samarium and europium (Urbain and Lacombe, Compt. rend. 1903, 137, 794; 1904, 138, 84, 1166; *cf.* Eberhard, Zeitsch. anorg. Chem. 1905, 45, 374).

Metallic samarium, m.p. 1300°–1400°, the hardest metal of the cerium group, is a light grey substance prepared by the electrolysis of the anhydrous chloride; it rapidly becomes tarnished with a layer of yellowish oxide.

Samarium carbide SaC_2. A yellowish crystalline mass, sp.gr. 5·86, produced by reducing samaria with carbon in the electric furnace (900 ampères, 45 volts), is decomposed by water evolving hydrogen, acetylene, olefines, and paraffins (Moissan, Compt. rend. 1900, 131, 924).

Samarium sulphide Sa_2S_3, yellow mass, sp.gr. 3·7, is obtained by passing sulphur vapour over the carbide (Annalen, 1908, 361, 190).

Samarium oxide (*Samaria*) Sa_2O_3, sp.gr. 8·347, is white with a yellowish tinge like the samarium salts of colourless acid radicles. The hydroxide is a gelatinous precipitate. A hydrated peroxide Sa_4O_9,xH_2O is produced by precipitating with ammonia in presence of hydrogen peroxide.

Samarium chloride $SaCl_3$, prepared by methods generally applicable for the anhydrous chlorides of rare earth metals (*v.* CERIUM, LANTHANUM, &c.) is a yellowish-white powder, sp.gr. 4·465, melting at 686° to a dark brown liquid. The dry salt absorbs ammonia forming a series of additive compounds, with 1, 2, 3, 4, 5, 8, 9·5, and 11·5 NH_3 (Compt. rend. 1905, 140, 141).

The **hydrate** $SaCl_3,6H_2O$, sp.gr. 2·382, crystallises in yellow plates, the **platini-** and **aurichlorides** are $SaCl_3,PtCl_4,10{\cdot}5H_2O$ and

$$SaCl_3,AuCl_3,10H_2O,$$

respectively (Cleve, Bull. Soc. chim. 1885, [ii.] 43, 53; Chem. News, 1886, 53, 30, 45, 67, 80, 91, 100; these memoirs contain descriptions of many other samarium salts).

Samarium dichloride $SaCl_2$, a dark brown crystalline mass, sp.gr. 3·687/22°, insoluble in alcohol, but decomposed by water yielding samaria, samarium oxychloride, and hydrogen, is of interest as being the only chloride of the rare earth series in which the metal is apparently bivalent; it is produced by reducing the anhydrous trichloride at high temperatures with hydrogen, ammonia, or aluminium powder. Samarium triiodide can be similarly reduced to the diiodide (Matignon and Cazes, Compt. rend. 1906, 142, 83).

Samarium sulphate $Sa_2(SO_4)_3,8H_2O$, sp.gr. 2·930/18°, forms light yellow crystals more sparingly soluble than neodymium and praseodymium sulphates. The double sulphates,

$$2Sa_2(SO_4)_3,9K_2SO_4,3H_2O,$$
$$Sa_2(SO_4)_3,Na_2SO_4,2H_2O, \text{ and}$$

$Sa_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$, are more soluble in aqueous alkali sulphates than the corresponding neodymium and praseodymium double salts (Ann. Chim. Phys. 1880, [v.] 20, 535; Compt. rend. 1881, 93, 63).

Samarium carbonate $Sa_2(CO_3)_3,3H_2O$, acicular crystals, obtained by treating with carbonic acid the hydroxide precipitated by ammonia. Alkali carbonates added to soluble samarium salts produce voluminous precipitates of the double alkali carbonates

$$Sa_2(CO_3)_3,R_2CO_3,xH_2O,[R{=}Na,K \text{ or } NH_4]$$

which gradually become crystalline.

Samarium acetylacetonate

$$Sa[CH(CO{\cdot}CH_3)_2]_3,$$

m.p. 146°–147°, prepared by the interaction of samarium nitrate, acetylacetone, and ammonia in aqueous solution, is somewhat more soluble in water than other acetylacetonates of the rare earth series; its molecular weight in carbon disulphide solution is double that indicated by the foregoing formula (Biltz, Annalen, 1904, 331, 334).

Absorption spectrum. Samarium salts exhibit a series of absorption bands ranging from λ559 to λ362, but concentrated solutions must be employed as the intensity of this spectrum is much less that that of neodymium or praseodymium (Demarçay, Compt. rend. 1900, 130, 1185).

Spark spectrum not very characteristic (Exner and Haschek, Sitzungsber. Wien. 1898, IIc. 108, 1106, 110, 504; Demarçay, Compt. rend. 1900, 131, 995). *Reversal spectrum* and *cathode luminescence* (Demarçay, *ibid.* 1900, 130, 1185). *Arc spectrum* (Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904). G. T. M.

SAMARSKITE. A complex rare-earth mineral consisting of columbate and tantalate of cerium and yttrium earths with ferrous oxide and 10–13 p.c. of uranium oxide. It breaks with a brilliant, conchoidal fracture, showing a velvet-black colour and pitchy lustre; sp.gr. 5·4–5·8. It is found as orthorhombic crystals embedded in felspar in the Ilmen Mountains, Urals, and in some abundance, as masses up to 20 lbs., in the Wiseman and Grassy Creek mica mines in Mitchell Co., North Carolina. Recently, it has been found as irregular fragments and masses up to 200 lbs. in pegmatite in the Sankara mica mine, Nellore district, Madras (G. H. Tipper, Rec. Geol. Survey, India, 1911, 41, 210). L. J. S.

SAMBUNIGRIN *v.* GLUCOSIDES.

SAMSONITE. An explosive consisting of nitroglycerin (57–60); nitro-cotton (3–4); potassium nitrate (17–19); wood meal (5–7); ammonium oxalate (12·5–14·5).

The same name has also been applied (Werner and Fraatz, Centr. Min., 1910, 331) to a mineral with the composition $2Ag_2S{\cdot}MnS{\cdot}Sb_2S_3$, found as small, monoclinic crystals in the Samson mine at St. Andreasberg in the Harz mountains. L. J. S.

SAMSU. A fermented drink of Eastern Asia made from rice.

SANATOGEN. A preparation consisting of a sodium casein compound of glycerophosphoric acid.

SAND. (*Sable*, Fr.) An accumulation of grains of mineral matter resulting from the disintegration of rocks. It is generally silicious, since quartz is the most abundant rock-constituent, and by its hardness and chemical stability survives after the associated minerals have disappeared. The microscopic studies of Sorby, Phillips, and others have shown that in some sands a growth of crystalline quartz surrounds the original water-worn grains, the secondary deposit and the nucleus being in optical continuity (Quart. Journ. Geol. Soc. 1880, 36, 46; 1881, 37, 21). In sands derived from granitic rocks and crystalline schists, the quartz is often associated with grains of felspar and scales of mica; and A. Dick has pointed out the occurrence in such sands of zircon, rutile, and tourmaline (Nature, 1887, 36, 61). Many sands are coloured yellow or brown by ferric hydrate, while others are speckled with dark-green grains of glauconite. 'Black sand' usually contains magnetite, ilmenite, or cassiterite; the titaniferous iron-sand of Taranaki, in New Zealand, and that of the coast of Labrador, have been used as ores. Sands rich in monazite (*q.v.*) supply practically the whole of this mineral used commercially. 'Gem-sands' vary in nature according to the character of the rocks which yielded them, but frequently contain garnets, spinels, and zircons. By systematically panning and examining the heavy residues or concentrates from river-sands, many useful minerals (gold, platinum, cassiterite, monazite, &c.) may be detected and traced to their sources. 'Volcanic sand' is composed of finely divided lava.

Most sands have been deposited as sediments in water, either fresh or salt; but there are also accumulations of wind-drifted materials, known as *Æolian sands*, occurring as dunes along the coast or in the interior of deserts. The grains of desert-sand are usually much more rounded than those of water-borne sand. Blown sand exerts considerable abrasive power, wearing any isolated rocks into characteristic forms. The eroding action of blown sand is taken advantage of in the *sand-blast*, introduced by B. C. Tilghman. By this process, glass and stone may be rapidly engraved or cut by the action of a jet of sand projected with great velocity by means of steam or compressed air.

Silicious sand, as free as possible from iron, is valued in the manufacture of glass. Glass-sand is dug near Reigate in Surrey, Lynn in Norfolk, &c., and is largely imported from Fontainebleau, in France. Excellent sand occurs at Gweedore, in county Donegal. Sand is also used in the preparation of mortar, sand-lime bricks, and artificial stone, for which purpose it should be sharp and clean; for polishing and scouring ('silver-sand'), and for a variety of purposes.

Sand is largely used as a moulding material for foundry work. The best moulding sand is argillaceous, containing in some cases as much as 6 p.c. of clay. Where a strong adhesive material is required, as for cores in casting, a clayey sand is especially needful. The foundry sand, or loam, is usually prepared by sifting, and may often be advantageously mixed with coke dust. Facing sand should be coated with carbonaceous matter, such as powdered charcoal or graphite.

Fulgurites, or 'lightning-tubes,' are occasionally formed when lightning strikes a sandy soil, the quartz becoming vitrified by the heat, and so forming natural tubes of silica-glass.

For a large collection of analyses of sands, *see* Mineral Resources of the United States, for 1909, 1911, part ii., p. 525. L. J. S.

SANDAL, SANDEL, or **SANTAL WOOD** *v.* SANDERSWOOD.

SANDALWOOD CAMPHOR *v.* CAMPHORS.

SANDARAC, SANDARACIN *v.* RESINS.

SANDERSWOOD (*Red Saunderswood, Santalwood, Sandelwood*). This dyestuff is classed along with *Barwood*, *Camwood*, and *Caliatour* or *Cariatour-wood*, since they all possess very similar dyeing properties, and, owing to the insolubility in water of the resinous colouring matters they contain, they are called the *insoluble red woods.* They cannot, therefore, be made to yield commercial extracts like the 'soluble red woods,' Brazilwood and its allies.

Santalwood is the product of *Pterocarpus santalinus* (Linn.), a papilionaceous tree growing in tropical Asia. It is imported from the East Indies, Ceylon, the coasts of Coromandel and Malabar, Golconda, Timor, Madagascar, &c. It occurs in commerce in the form of hard, heavy billets of a dull-red colour. In the state of powder it gives off a faint aromatic odour like that of orris root, specially noticeable when it is heated, or boiled with water. It yields to alcohol about 16 p.c. of colouring matter (Pelletier), insoluble in cold water, sparingly soluble even in boiling water, but very soluble in alcohol, ether, acetic acid, and the caustic alkalis.

Barwood is the wood of a fine large tree, *Baphia nitida* (Lodd.), and is imported from the west coast of Africa, *e.g.* Sierra Leone, Angola, &c. In the log its physical properties are generally similar to those of santalwood; in the rasped condition it has a somewhat brighter red colour, and it is devoid of aromatic odour. Boiling water extracts about 7 p.c. colouring matter, alcohol about 23 p.c., and hydrated ether about 19 p.c. (Girardin and Preisser). In caustic alkalis the colouring matter is readily soluble, with a reddish-purple colour, and is precipitated therefrom on addition of acids. Acetic acid gives a dark-brown coloured extract.

Camwood, stated by some to be derived from a variety of *Baphia nitida*, is a dyewood similar in general properties to those already mentioned, but somewhat more expensive and yielding deeper shades in dyeing. Its colouring matter seems to be present in larger amount, or it is more soluble than in the other woods. It is imported from the west coast of Africa, the Gaboon and Congo rivers, &c.

Caliatour-wood seems to be a somewhat more expensive variety of sanderswood, and possesses a similar aromatic odour. It is imported from the East Indies, and goes chiefly to the Continent.

The chemistry of these dyewoods is unsatisfactory, being incompletely studied, but from our present knowledge concerning their application in dyeing, the useful colouring principles they contain are evidently very closely related to each other.

Sandel-red is the name given to the red resinous colouring principle first obtained by Pelletier on the evaporation of an alcoholic extract of sanderswood.

Santalic acid or *santalin*, obtained by Meier, is a purer form of 'sandel-red.' It is prepared by extracting sanderswood with ether, and evaporating the solution to crystallisation. The impure product thus obtained is washed with water, dissolved in alcohol, and precipitated with an alcoholic solution of lead acetate. The precipitate is well washed with boiling alcohol, then suspended in alcohol, and decomposed by dilute sulphuric acid; the filtrate from the lead sulphate is then evaporated to crystallisation. Thus obtained, Meier's santalin forms minute red crystals (m.p. 104°), insoluble in water, but very soluble in alcohol with a blood-red colour; soluble also in ether with a yellow colour, which becomes red on exposure to air. It dissolves in acetic acid, also in concentrated sulphuric acid with a dark-red tint, and in caustic alkalis with a purple colour. The formulæ assigned to santalic acid are $C_{15}H_{14}O_5$ (Weyermann and Häffely), and $C_{16}H_{16}O_3$ (Pelletier).

Santalic oxide is a substance extracted by Meier along with the santalic acid by means of alcohol. By extraction with water he obtained other bodies, which were named *santalide*, *santaloïde*, *santalidide*, and *santaloïdide*. All these are amorphous resinous substances whose existence as distinct chemical individuals is very doubtful.

Bolley prepared the colouring matter of sanderswood by exhausting it with alcohol and precipitating the concentrated solution by addition of water; also by extracting the wood with dilute caustic alkali, precipitating with acid, dissolving the precipitate in alcohol, and precipitating the solution with water. From analyses of several samples of colouring matter prepared according to these two methods, Bolley concluded that the colouring matter exists in two states of oxidation, according as it is obtained from young and pale-coloured wood, or such as is old and dark coloured; prepared from the latter he found it to contain more oxygen and less hydrogen. He noted further that alkaline solutions of the colouring matter become darker coloured on exposure to air, evidently because oxygen is absorbed. Other observers have remarked that the freshly-cut young branches of sanderswood exhibit in their interior a yellow colour, which only becomes red on exposure of the sections to the atmosphere.

Wimmer states that santalin is accompanied by a brown-coloured bitter principle soluble in boiling water, also a brown resinous colouring matter, *santalidine*, more soluble in the various solvents than santalin, of which it appears to be an oxidation product.

Santal was obtained by Weidel by extracting sanderswood with dilute caustic alkali, and neutralising the filtered solution with hydrochloric acid. The voluminous brick-red precipitate thus obtained was washed, dried, and extracted with ether. The dark-red ethereal solution was concentrated, mixed with alcohol, and then allowed to evaporate spontaneously, when almost colourless crystals of santal separated. These were purified by washing with a little alcohol and recrystallising. This method yielded about 1½ grms. santal per pound of wood. Santal crystallises from hot alcohol as colourless, lustrous, iridescent, quadrangular plates, to which the formula $2C_8H_6O_3, 3H_2O$ was assigned. It is insoluble in hot water, carbon disulphide, benzene, or chloroform, and only slightly soluble in alcohol or ether. It dissolves somewhat sparingly in ammonia, but very readily in dilute caustic potash or soda, with a pale-yellow colour. Its alcoholic solution assumes a red colour on addition of ferric chloride. In concentrated sulphuric acid santal dissolves with a lemon-yellow colour. Nitric acid gives an olive-coloured solution, from which water precipitates yellow flocks. With bromine santal yields a granular crystalline product slightly soluble in alcohol. When santal is fused with caustic potash until the melt no longer dissolves in water with a red colour, it yields protocatechuic acid. Weidel considers santal to be isomeric with, and probably closely related to, piperonal.

By the further and long-continued extraction with ether of the brick-red resinous precipitate, *sandelwood resin*, thrown down by acid from the above-mentioned alkaline extract of the wood, J. Weidel obtained in small quantity a substance $C_{14}H_{12}O_4$. On evaporating the ethereal solution it was deposited as a red crystalline powder, having a green metallic lustre. It is insoluble in boiling water, very slightly soluble in ether or even in hot alcohol; in the latter with a red colour. In ammonia and the caustic alkalis it dissolves with a reddish-purple colour, from which calcium chloride precipitates a purple precipitate. In concentrated sulphuric acid it dissolves with an orange colour.

It has been suggested that Weidel's santalin is a purer form of the resinous colouring matters analysed by Bolley, Weyermann, and Häffely, and is probably produced during the oxidation of santal in alkaline solution. Sandelwood resin when heated with zinc-dust yields a small quantity of an oily distillate in which no anthracene can be detected. Fused with caustic alkali, it yields catechol and resorcinol. Judging from its slight solubility in alcohol and its characteristic green metallic lustre, Weidel's substance $C_{14}H_{12}O_4$ can, however, hardly be identical with the santalin or santalic acid of Meier. A partial repetition of Weidel's investigation was subsequently carried out by A. Herz and A. G. Perkin (employing, however, barwood), and as a result the individuality of the substances described by this author has been confirmed. Whereas by this method santal was produced in some quantity, the crystalline colouring matter '$C_{14}H_{12}O_4$' could only be isolated in extremely meagre amount. Incidentally also the well-defined compounds *Pterocarpin* and *Homopterocarpin* of Caseneuve and Hugounenq (*see* below) were isolated from sanderswood.

Franchimont and Sicherer, by adopting a method similar to Meier's, but extracting in the first instance with alcohol instead of ether, boiling the product eventually obtained with hydrochloric acid, and crystallising from dilute alcohol, obtained from sanderswood, and more abundantly from caliatour-wood, an amorphous colouring matter $C_{17}H_{16}O_6$ (m.p. 104°–105°), apparently identical with santalin. It is readily soluble in alcohol, acetic acid, caustic and carbonated alkalis, sparingly soluble in ether, and insoluble in chloroform or carbon disulphide. Fused with caustic potash it yields acetic acid, resorcinol, and probably also protocatechuic acid and catechol, together with a minute quantity of a volatile product smelling like rosewood.

Heated to 180° with concentrated hydrochloric acid, it yields methyl chloride; alcohol dissolves from the residue in the tube a substance $C_8H_{10}O_5$, and leaves behind a lustrous black mass soluble in caustic alkalis; ether withdraws from the hydrochloric acid solution a substance crystallising in colourless needles. The same substance is obtained by diluting the hydrochloric acid with water and distilling. The distillate gives with bromine water a precipitate of lustrous needles, m.p. 81°.

When the original colouring matter is boiled with dilute nitric acid it yields oxalic acid and a yellow bitter substance, probably picric or styphnic acid. By oxidation in alkaline solution with potassium permanganate it yields a crystalline substance having a strong odour of vanillin, also oxalic and acetic acids.

Anderson extracted ground barwood with anhydrous methylated ether free from alcohol. At first the solution is dark red, but ultimately it becomes almost colourless. By spontaneous evaporation of the concentrated ethereal solution a small quantity of *baphic acid* is deposited in the form of tabular crystals. After further evaporation, mixing the concentrated extract with alcohol, and allowing to stand for some days, there is deposited a crystalline magma of *baphiin* contaminated with a solid red colouring matter and some dark viscous colouring matter not yet examined.

After exhaustion with ether the wood is extracted with alcohol, and after highly concentrating the solution it is left at rest for some time, when it congeals to a semi-crystalline mass which contains a viscous red colouring matter and a crystalline constituent not examined.

Baphiin $C_{24}H_{20}O_8$ (m.p. about 200°) crystallises from alcohol in the form of lustrous tabular crystals having an odour of orris root; from ether it crystallises in tufts of needles. It is insoluble in water, and very sparingly soluble in benzene or in carbon disulphide. In alcoholic solution it rapidly oxidises on exposure to air, producing orange-red or pale-purple colours.

Baphic acid $C_{24}H_{22}O_9$ or $C_{24}H_{22}O_{10}$ is prepared by boiling baphiin with dilute caustic potash, and adding hydrochloric acid, when it is thrown down as a yellowish-white precipitate. Crystallised from ether it forms white nacreous scales, very soluble in ether, slightly less so in alcohol, and insoluble in water.

Baphinitin $C_{24}H_{24}O_6$ is thrown down as a crystalline precipitate on the addition of water to the filtrate from the precipitate of lead baphate which is formed on mixing alcoholic solutions of baphiin and lead acetate. It is also the chief product of the action of boiling dilute caustic potash on baphiin. Baphinitin forms white needles, soluble in alcohol or in ether, but insoluble in water; it has the same odour as baphiin but stronger.

Baphinitone $C_{26}H_{26}O_6$. On boiling baphiin with a strong aqueous solution of caustic potash without access of air, an insoluble residue is left which contains three substances: (1) baphinitin, moderately soluble in alcohol or ether; (2) baphinitone, very readily soluble in these liquids; (3) a small quantity of an unexamined substance, m.p. 164·1°, very sparingly soluble even in hot alcohol, and separating therefrom in granular crystals. Baphinitone is extracted from the above-mentioned residue insoluble in caustic potash, by treating it with cold alcohol in which it readily dissolves along with a very small amount of baphinitin. The solution is evaporated, and the treatment with alcohol is repeated until the crystals thus obtained, after drying over sulphuric acid, have a melting-point of about 88°. Baphinitone crystallises from alcohol in hemispherical masses composed of white lustrous radiating crystals insoluble in water.

Tribromo-baphinitone $C_{26}H_{23}Br_3O_6$ is obtained by mixing ethereal solutions of baphinitone and bromine; on evaporating off the ether it remains as a white substance, which may be purified by washing with alcohol or ether, in which it is almost insoluble. It separates from a hot ethereal solution in small granules, which melt with sudden blackening at 180·2°.

Baphiin, baphinitone, and substance (3) above referred to, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red colour is obtained, which changes gradually to green. From the description given by Anderson of these substances it seems possible that whereas baphiin may be santal, baphinitin and baphinitone in reality respectively consist of pterocarpin and homopterocarpin.

In addition to the above-mentioned substances, barwood contains, according to Anderson, at least three colouring matters. Ether extracts from the wood two of these: one (*a*) which is less soluble, and which tenaciously adheres to the baphiin, and another (*b*) which is more soluble and easily removed from it. When the extraction with ether is completed, alcohol will dissolve out a third colouring matter (*c*). All are insoluble in benzene, and give purple lakes with lead acetate, and purple solutions with alkalis.

The solubility in ether of the colouring matter (*a*), which is a bright-red powder, diminishes after exposure to air. Any adhering baphiin is removed from it by means of boiling benzene. The colouring matter (*b*) is crystalline, and dissolves readily in boiling alcohol; if hydrochloric acid be added to the solution the colour becomes darker, if then ammonia or caustic potash be added the colour changes to deep pink, whereas the final colour of the solution of the colouring matter (*c*) under similar treatment is deep purple.

According to A. G. Perkin (Chem. Soc. Trans. 1893, 63, 975) an alcoholic solution of commercial santalin gives with potassium acetate a deep maroon-coloured precipitate.

This which appears to be a potassium salt of the colouring matter has the composition

$$C_{30}H_{27}O_{10}K.$$

Cochenhausen (Zeitsch. angew. Chem. 1904, 17, 883) considers that santalin does not exist in the fresh plant in the free condition, but as glucoside. The young branches of the *Pterocarpus santalinus*, for instance, possess in the centre a yellow colour, which on exposure to air develops a red tint (*cf.* Bolley, *l.c.*).

Cain and May (preliminary communication, Seventh Annual Congress of Applied Chemistry, 1909, iv. B. 85) isolated santalin from sanderswood by Meier's method (*l.c.*), and describe it as red microscopic needles, m.p. 215°. From the results of their analyses these authors conclude that the correct formula of santalin is given by Weyermann and Häffely (*l.c.*) $C_{15}H_{14}O_5$, and that the substance contains one methoxy group.

Pterocarpin $C_{20}H_{16}O_6$ is a crystalline substance, different from Weidel's santal, obtained by Cazeneuve and Hugounenq from sandelwood, to the amount of about 0·1 p.c., as follows. The rasped wood mixed with one-fourth its weight of slaked lime is made into a paste with water, then dried and extracted with ether containing alcohol. On evaporating the solution a crystalline deposit is obtained, which, when recrystallised from ether, yields a mixture of platy crystals of *Pterocarpin* and long needles of *Homopterocarpin*, only the latter of which dissolves readily in carbon disulphide.

Pterocarpin, m.p. 152°, is insoluble in water, also in acids and alkalis; it is soluble in cold, better still in hot alcohol, but is only sparingly soluble in ether. It crystallises from chloroform in small rhombic prisms, and turns the polarised ray to the right. It appears to be a lower homologue of homopterocarpin. Pterocarpin in carbon disulphide solution gives with bromine a derivative

$$C_{20}H_{15}BrO_6,$$

m.p. 93°, crystallising from benzene alcohol in yellowish needles.

Homopterocarpin $C_{24}H_{24}O_6$, m.p. 82°–86°, is sparingly soluble in cold alcohol. It turns the polarised ray to the left. Caustic potash has no action upon it, but heated with hydrochloric acid in sealed tubes to 120° it yields methyl chloride and resorcinol ether $(C_6H_4{\cdot}OH)_2O$. When boiled with fuming nitric acid it yields oxalic acid and two trinitro-orcinols, of which one forms yellow needles, m.p. 162°, the other is liquid. With excess of bromine homopterocarpin yields leafy crystals of $C_{24}H_{18}Br_6O_6$, m.p. about 270°, and with 2 mols. bromine to 1 mol. homopterocarpin dissolved in chloroform, colourless crystals of $C_{24}H_{23}BrO_6$ are obtained. The authors believe that homopterocarpin contains a kind of poly-orcin,

$$(3[C_7H_5(OCH_3)(OH)_2]-3H_2O).$$

A. Zander (1886) patented a method of rendering soluble the colouring matter of sanderswood and its allies, by treating the resinous colouring matter in the cold with fuming sulphuric acid, until a sample of the mixture dissolves in water, from which the new colouring matter is precipitated by means of common salt. The method does not appear to have any practical value.

The well-known *narra* wood, *Pterocarpus* spp. of the Philippines, may be considered as a variety of sanderswood, as it contains pterocarpin, homopterocarpin, and a colouring matter *narrin* very similar to, but not identical with, santalin (Brooks, Philippine Journal of Science, 1910, 5, 439).

Narrin obtained as a dark red amorphous powder, does not melt but swells with charring at about 180°. It dissolves in alkaline solutions, and these are decolourised by zinc-dust, although the colour reappears on oxidation with air. Distilled with zinc-dust resorcinol dimethyl ether is obtained, and by fusion with alkali phloroglucinol and resorcinol are produced. Slow oxidation of narrin with alkaline potassium permanganate yielded only vanillin. The dyeing properties of narrin are similar to those of santalin, but a marked distinction is observed as regards the composition of the copper salts of these colouring matters. Thus whereas santalin gives the copper salt $(C_{15}H_{13}O_5)_2Cu$ (Cu=10·34 p.c.) corresponding to the potassium salt described by Perkin, the corresponding narrin derivative contains but 6·26 p.c. of copper.

Pterocarpin melts at 163° (not at 152° as previously stated), and molecular weight determinations indicate that its true formula is in reality $C_{14}H_{12}O_4$.

Homopterocarpin melts at 86°, possesses the formula $C_{17}H_{16}O_4$ (not $C_{24}H_{24}O_6$, *l.c.*), and when fused with alkali gives resorcinol. Hydriodic acid also forms resorcinol, and by distillation with zinc-dust resorcinol dimethyl ether is produced.

Employment in dyeing. In India it is said that sanderswood, with the addition of one-tenth of its weight of sapanwood, is employed in dyeing silk and cotton. In Europe, however, these dyewoods are never used in silk dyeing, but chiefly in the dyeing of wool, and occasionally cotton, for which latter barwood is exclusively employed.

In wool-dyeing various shades of brown are obtained by first boiling the wool in a bath containing the ground dyewood for 1–1½ hours and then adding to the same bath a solution of one or other of the following mordants: potassium dichromate, ferrous sulphate, copper sulphate, alum. During the first part of the operation, termed 'stuffing,' the wool absorbs a considerable amount of the resinous colouring matter and thus acquires an orange or reddish-brown colour; during the second part, this combines with the metallic oxide or mordant, and in the case of the three first-mentioned metallic salts the colour is changed to a very dark brown. Hence this part of the operation is termed the 'saddening.' The same results are more rationally obtained by employing two separate baths, since then the unexhausted baths may be replenished and used again. If the mordanting operation precedes the boiling with dyewood, similar but less intense, and not such level, shades are obtained. By adding logwood, fustic, and other dyewoods along with the sanderswood, &c., a variety of browns, olives, &c., may be obtained.

In dyeing vat-indigo blues on wool, sanderswood and barwood are commonly employed for the purpose of 'bottoming.' Before or after dyeing in the vat, but usually before, the woollen material is boiled in a bath containing the barwood or sanderswood; occasionally, the wool is mordanted. The object of the dyer is to impart a purplish hue to the indigo blue, thereby to intensify the colour somewhat, and to cause the colour to be less liable to rub off, or to wear grey at the seams in the case of clothing. The two latter points may probably be gained just as well by merely boiling the wool in water only, previous to dyeing in the vat. In this manner the wool is equally well softened and rendered more absorbent, so that the vat solution penetrates the fibre more thoroughly, and thus the precipitated indigo ultimately formed is enclosed within the substance of the fibre, and not so apt to rub off. The utility of the presence of the barwood in the bath, except for the purpose of modifying the shade of blue, is very questionable.

Barwood-red on cotton, also called sometimes 'mock Turkey-red,' is a bluish red of medium brilliancy. It is produced by first working the cotton in a cold decoction of tannin matter—*e.g.* sumach—then mordanting it by working in a cold weak solution of stannic chloride or nitro-muriate of tin, and, after washing, boiling in a bath with ground barwood.

All the colours produced from these dyewoods, whether on wool or cotton, are not fast to light. Those obtained on wool with the use of mordants are fast to milling; although the colours do not 'bleed,' alkalis tend to alter the hue of the colours and to render them more purplish.

At the present time these dyewoods are being rapidly superseded by the alizarin colours, and are now employed only to a limited extent.

A. G. P.

SANDIVER. (Fr. *Suint de verre.*) The scum formed on the surface of the molten glass in the glass pots; known also as *glass gall* (*v.* GLASS).

SANDMEYER REACTION *v.* DIAZO COMPOUNDS.

SANDSTONE. (*Grès*, Fr.). A granular silicious rock, consisting of consolidated sand. If the cohesion is imperfect, the friable mass is sometimes known as *sand-rock*. The consolidation of the sand may be effected either by pressure, or by deposition of mineral matter forming an agglutinating medium between the grains. When the cement is silicious, the resulting rock has great hardness and durability, but is difficult to work. Where the grains of sand are united by calcium carbonate, a *calcareous sandstone* is produced; such a rock may be readily worked as a freestone, but by weathering it is apt to lose the calcareous cement, and, becoming more or less cavernous in texture, tends to suffer disintegration. In an *argillaceous sandstone* the cement is clayey, and the stone is not generally durable as a building material. In a *micaceous sandstone* scales of mica are present, and in many cases facilitate the splitting of the stone along the planes of bedding, as in the Yorkshire flagstone. A *felspathic sandstone* contains grains of felspar, either crystalline or more or less kaolinised; much of the millstone grit of England is of this character, having clearly resulted from the disintegration of granitic rocks. The term *arkose* is often applied to a sedimentary rock made up of the constituent minerals of granite, rearranged by deposition in water.

Many sandstones—especially those of the Old Red Sandstone, the Permian, and the Trias—present various tints of red and brown, due to the presence of ferric oxide, or its hydrate, acting as a cement, and forming a thin pellicle around each grain of quartz. Green sandstones, such as those of the Upper Greensand of Surrey, owe their colour to dark grains of glauconite, generally the internal casts of the chambers of foraminifera. The bluish and greyish tints of many sandstones are referred to the presence of ferrous carbonate, or of finely-divided iron-pyrites, or even to iron phosphate. Sandstones which are 'blue hearted' usually assume yellow or brown tints where exposed to oxidising influences. Grains or crystals of iron-pyrites in a sandstone are apt to produce rusty blotches when weathered. (On the colour of sandstones *v.* G. Maw, Quart Journ. Geol. Soc. 1868, 24, 351.)

If the component grains of silica are sharp, the rock is termed a *grit*; many grits are valued as grindstones, while if very fine in texture they may sometimes be used as whetstones. A coarse grit, with large grains of quartz, may be employed as a millstone.

It has been shown by F. Clowes (Proc. Roy. Soc. 1889, 44, 363; 1899, 64, 374) that in certain Triassic sandstones, like the 'hemlock stone,' near Nottingham, the grains of sand are united by barium sulphate. Certain sandstones are impregnated with metallic compounds, rendering them useful as ores: thus, the Lower Keuper sandstones of Alderley Edge and of Mottram St. Andrew's, in Cheshire, have yielded copper carbonates, both green and blue, with galena and cerussite, cobalt and manganese ores, and vanadinite. The workable part of the metalliferous sandstone contained an average of 1·4 p.c. of copper; this was dissolved out by dilute hydrochloric acid, and precipitated by scrap iron (Greenwell, Proc. S. Wales Inst. Eng. 1866, 4, 44; Hull, Geol. Mag. 1864, 1, 65). Native copper is disseminated in a granular form through certain sandstones at Lake Superior. The Bunter sandstone, near Commern, in the Eifel, contains valuable deposits of lead-ore, usually sulphide, although sometimes carbonate, occurring in nodules, whence the rock is termed *Knottensandstein.* Many iron ores of the secondary rocks, like those of Northamptonshire and Lincolnshire, are so silicious as to pass into highly ferruginous sandstones. (For analyses of sandstones, *v.* J. A. Phillips, Quart. Journ. Geol. Soc. 1881, 37, 21; J. A. Howe, The Geology of Building Stones, London, 1910; J. Watson, British and Foreign Building Stones, Cambridge, 1911; for American sandstones *v.* G. P. Merrill, Smithsonian, Rep. for 1886, part 2, 443; Stones for Building and Decoration, 3rd ed., New York, 1903.) F. W. R.

SANGUINARIA. *Bloodroot.* The rhizome of *Sanguinaria canadensis* (Linn.) contains an alkaloid, *Sanguinarine* $C_{17}H_{15}NO_4$, said to be identical with *Chlererythrine*, obtained from celandine (*Chelidonium majus* [Linn.]) (*v.* Naschold, J. pr. Chem. [i.] 106, 385).

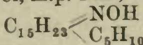
SANIDINE *v.* FELSPAR.

SANOFORM *v.* SALICYLIC ACID and SYNTHETIC DRUGS.

SANTALENE $C_{15}H_{24}$ is contained in East Indian sandalwood oil (*Santalum album* [Linn.]). It is a mixture of the isomeric α- and β-santalenes.

α-Santalene is a tricyclic sesquiterpene; it forms a colourless oily liquid with a faint odour, b.p. 118°–120°/9 mm., sp.gr. 0·8984 at 20°, α_D −15° (100 mm. tube). When oxidised with ozone, it yields *tricyclic eksantalal* $C_{11}H_{16}O$, and when treated with glacial acetic acid in a sealed tube at 180°–190° it forms an *α-acetate*, b.p. 164°–165°/14 mm.

α-Santalene also yields an *α-nitrosochloride* $C_{15}H_{25}NOCl$, m.p. 122°, and an *α-santalenenitrolpiperidine* $C_{15}H_{23}{<}\begin{matrix}NOH\\C_5H_{10}N\end{matrix}$, m.p. 108°–109°.



β-Santalene is a bicyclic sesquiterpene and closely resembles the α- compound, b.p. 125°–127°/9 mm., D_{20} 0·892, α_D −35°, when oxidised with ozone it yields *bicyclic eksantalal*, and treated with glacial acetic as above it gives a *β-acetate* $C_{15}H_{25}O{\cdot}COMe$, b.p. 164°–168°/14 mm. β-Santalene yields two *nitrosochlorides*, m.p. 152° and 106° respectively, the former being less soluble in alcohol than the latter. Each of these nitrosochlorides yields a *nitrolpiperidine*, m.p. 101°, and 104°–105° respectively.

When β-santalene is treated with glacial acetic acid and sulphuric acid, it yields a *sesquiterpene alcohol* $C_{15}H_{25}OH$, which has a strong odour of cedar and has b.p. 160°–165°/6 mm.

Santalene dihydrochloride $C_{15}H_{24},2HCl$, obtained by the addition of hydrogen chloride to santalene in methyl alcohol has b.p. 140°–142°/0·55 mm., and sp.gr. 1·076 at 20°. When boiled with alcoholic potash, it yields β-santalene. When treated with sodium and boiling alcohol the dihydrochloride yields a mixture of hydrocarbons which when treated with ozone gives pure *tetrahydrosantalene* $C_{15}H_{28}$, b.p. 116°–118°/9 mm., sp.gr. 0·864 at 20°, α_D +7° 30′ (100 mm. tube). This hydrocarbon is dicyclic and is analogous to dihydroeksantalol and to dihydroeksantalic acid (Semmler, Ber. 1910, 43, 445).

Literature on the santalenes: Soden and Müller, Pharm. Zeit. 1899, 44, 258; Chem. Zentr. 1899, i. 1082; Arch. Pharm. 1900, 238, 149, 353; Guerbet, Compt. rend. 1900, 130, 417, 1324; Semmler, Ber. 1907, 40, 3321.

SANTALIC ACID. *Santalin v.* SANDERSWOOD.

SANTALOL $C_{15}H_{23}OH$, often known in commerce as *Gonorol*, is the chief constituent of East Indian sandalwood oil from which it is obtained by distilling the latter in steam, converting the oil in the distillate into the hydrogen phthalate and then hydrolysing this ester: or sandalwood oil is saponified and the product submitted to fractional distillation *in vacuô*, or with superheated steam. By simple fractional distillation, the alcohol cannot be obtained pure (D. R. PP. 110485, 116815; Frdl. 1897–1900, 917; *see* also Soden, Arch. Pharm. 1900, 238, 353; Müller, *ibid.* 366).

Thus obtained it has b.p. 161°–168°/10 mm., sp.gr. 0·973 at 20°, α_D −21° (100 mm. tube). By repeated fractionation it can be separated into its two chief constituents, the isomeric α- and β-santalols.

α-Santalol is the chief constituent of commercial santalol. It is a tricyclic sesquiterpene alcohol, b.p. 301°–302°, 159°–160°/10 mm., sp.gr. 0·978 at 20°, $[\alpha]_D$ +1° to +2°.

β-Santalol is a bicyclic sesquiterpine alcohol, b.p. 309°–310°, 167°–168°/10 mm., sp.gr. 0·9715 at 20°, α_D −42° (Guerbet, Compt. rend. 1900, 130, 1324; Semmler, Ber. 1910, 1894).

When crude santalol is oxidised with potassium permanganate santalal and eksantalic acid are formed as chief products.

Santalal, santalaldehyde $C_{15}H_{22}O$, has b.p. 152°–155°/10 mm., sp.gr. 0·995 at 20°, α_D +13° to +14°, and contains a very small quantity of *l*-santalal. *Santalal semicarbazone* has m.p. 230°, and the *oxime* m.p. 104°–105°, b.p. 182°–185°. When the latter is boiled with acetic anhydride it yields the *nitrile* $C_{15}H_{21}N$, b.p. 162°–166°/9 mm., sp.gr. 0·990 at 20°, α_D +14°, which when saponified gives *santolic acid* $C_{15}H_{22}O_2$, b.p. 192°–195°/9 mm.

When crude santalol is oxidised with ozone and the product distilled with steam, *eksantol oxide*, m.p. 157°, and chiefly *eksantalal* $C_{12}H_{18}O$, b.p. 109°–110°/10 mm., are formed. By a similar process to that described above, it can be converted into *eksantalic acid* $C_{12}H_{18}O_2$, m.p. 68°, b.p. 161°–163°/10 mm. This acid is also formed as above and as a by-product in the oxidation of santalol with ozone. By the reduction of its methyl ester, *dihydroeksantalic acid* is formed, b.p. 164°–166°/10 mm., m.p. 58°, the methyl ester of which when reduced yields *dihydroeksantalol* $C_{12}H_{22}O$, b.p. 130°–132°.

When eksantalal is treated with acetic anhydride it forms an *enol acetate*, which on oxidation with potassium permanganate yields *noreksantalic acid* $C_{11}H_{16}O_2$, m.p. 93°, b.p. 143°–145°/10 mm.; the methyl ester of this acid gives on reduction *noreksantalol* $C_{11}H_{18}O$, b.p. 114°–117°/10 mm., which when oxidised with chromic acid gives *noreksantalal*, m.p. 92°–94°. This yields an enol acetate, b.p. 110°–113°/10 mm., which, when oxidised with permanganate in aqueous acetone, gives *teresantalic acid* $C_{10}H_{14}O_2$, m.p. 156°, and from this by reduction *teresantalol* $C_{10}H_{16}O$, m.p. 114°, is obtained. All these derivatives are tricyclic or α- compounds, but may in many cases be converted into the corresponding bi-cyclic or β- compound, by treatment with hydrogen chloride and subsequent saponification (Semmler and Zaar, Ber. 1910, 43, 1890; Semmler, *ibid.* 1722, 1893; *see* also Semmler, *ibid.* 1909, 42, 584; *ibid.* 1908, 41, 1488; *ibid.* 1907, 40, 1120; Semmler and Bartelt, *ibid.* 1907, 40, 3101, 4465; *ibid.* 1908, 41, 385, 866; Chapman and Burgess, Chem. Soc. Trans. 1901, 134; Müller, *l.c.*).

In addition such hydrocarbons as *noreksantalane* $C_{10}H_{16}$, &c., have been obtained from santalol (Semmler and Bode, Ber. 1907, 40, 1124).

When heated in a sealed tube with alcoholic potash, α-santalol yields *eksantalol* $C_{12}H_{20}O$.

Santalyl halides are obtained by treating santalol or sandal-wood oil with phosphorus halides or with phosgene in presence of bases, or by heating santalol halogen carbonate (D. R. P. 203849; Frdl. 1907–10, 918; Semmler and Bode, *l.c.*).

Santalyl chloride is an oil, b.p. 162°–167°/15 mm. pressure. The halides are used in perfumery and in medicine.

Santalyl carbonate is prepared by heating together equal parts of guaiacol carbonate and santalol *in vacuô* at 170°–180° until no more guaiacol distils over or by heating santalol

(200 grms.) with phenyl carbonate (100 grms.) and caustic soda (2 grms.) under diminished pressure at 140°–175°. The carbonate is then purified by washing and redissolving in dilute alcohol (Eng. Pat. 20586, 1906).

Santalyl ethyl carbonate is prepared by condensing santal oil with ethyl chlorocarbonate in pyridine. It boils at 180°–185°/25 mm., and has sp.gr. 1·010 at 15°.

Santalylacetyl carbonate, formed by the action of a chloroform solution of santalol on salacetyl chlorcarbonate, in the presence of pyridine, is a pale yellow syrupy liquid, with a faint aromatic odour soluble in chloroform, benzene, and ether, almost insoluble in water (D. R. P. 206055; Frdl. 1907–10, 944).

The santalyl esters of the fatty acids $C_nH_{2n}O_2$ and $C_nN_{2n-2}O_2$ (where n=not less than 5) are prepared in the ordinary way and are said to be free from the objectionable taste of santalol, and of its esters with the lower fatty acids (D. R. P. 182627; Frdl. 1905–7, 942). For some of the lower esters *see* D. R. PP. 201369, 191547.

Mixed santalyl esters of dibasic acids are obtained by heating santalol with the anhydride of the required acid at 100°–120°, and then alkylating the resulting santalyl acid (D. R. P. 208637; Frdl. 1907–10, 922).

Methylsantalylsuccinate is an oil of sp.gr. 1·058 at 25°.

Methylsantalylphthalate has sp.gr. 1·085, and methyl *santalylcamphonate* has sp.gr. 1·04 (*see* also D. R. P. 193960).

The santalyl esters of monobasic aromatic acids are prepared by the action of the acid chlorides, anhydrides or esters on santalol. They are non-irritant and do not possess the disagreeable taste of santalol or of its acetyl and phthalic acid derivative (D. R. PP. 173240, 18725; Frdl. 1905–7, 939, 941).

The *santalyl ester of allophanic acid*

$$C_{15}H_{23}\cdot CO_2\cdot NH\cdot CO\cdot NH_2$$

is prepared by the prolonged action of cyanic acid on santalol in benzene solution or by the action of urea chloride, phenol carbonate or phenol allophonate on santalol (D. R. P. 204922; Frdl. 1907–10, 921). It melts at 162° and is tasteless and odourless, is soluble in most organic solvents, but not in water.

Santalyl ethers are obtained by treating santalyl halides with metal alcoholates or by treating santalol or sandalwood oil with alkylating agents (D. R. P. 202352).

Santalyl methyl ether, b.p. 149°–156°/16 mm., and *santalyl ethyl ether*, b.p. 169°–174°/22 mm., are colourless liquids.

Santalyl phenyl ether, b.p. 232°/20 mm., is a viscid oil, and the *menthyl ether*, b.p. 201°–210°/5 mm., is a colourless syrup.

Santalol combines with formaldehyde in presence of dilute mineral acids at 95°–100°, forming the compound $C_{16}H_{18}O_2$, a yellow balsam-like oil of antiseptic properties, sp.gr. 0·882 $[\alpha]_D 10{\cdot}9°$ at 20° in chloroform. When distilled with warm water it decomposes into its constituents (D. R. P. 148944; Frdl. 1902–4, 69).

The *dialkyl aminoacetyl santalols*, obtained by the action of halogen acetyl santalol on secondary amines, are said to be valuable in medicine owing to the fact that they form solid, odourless and readily assimilated salts (D. R. P. 226229; J. Soc. Chem. Ind. 1910, 1474).

SANTENE C_9H_{14} is a terpene contained in sandalwood oil (*Santalum album*, Linn.) (Müller, Arch. Pharm. 1900, 238, 366), in various pine needle oils, *Picea excelsa* (Link), and other oils (Aschan, Ber. 1907, 40, 4918). Santene may also be obtained by treating teresantalic acid with dilute sulphuric acid (Semmler, *ibid.* 4591), or by chlorinating π-norborneol and then splitting off hydrochloric acid (Semmler and Bartelt, *ibid.* 4466; *ibid.* 1908, 41, 125). Santene is optically inactive, has b.p. 31°–33°/9 mm., sp.gr. 0·863 at 20°, n_D 1·46658.

When oxidised in benzene solution with ozone or potassium permanganate, it yields *santene diketone* $C_9H_{14}O_2$, b.p. 124°–127°/9 mm., sp.gr. 1·024 at 20°, n_D 1·46658, its *dioxime* has m.p. 129° and the disemicarbazone has m.p. 216°. The diketone is oxidised by alkaline bromine solution to a *keto acid* $C_8H_{12}O_3$, b.p. 173°–175°/10 mm., yielding a semicarbazone, m.p. 182°. A series of other octene derivatives have been obtained from the diketone (Semmler and Bartelt, Ber. 1907, 40, 4595; *ibid.* 1908, 41, 869).

When treated with formic acid, santene yields π-norborneol formate, b.p. 82°–84°/9 mm., which, except for its being optically inactive, is identical with the product obtained by the interaction of teresantalic and formic acid (*ibid.* 125, 385).

Santenol acetate $C_9H_{15}O\cdot C_2H_3O$ is obtained by treating santene with glacial acetic and dilute sulphuric acids. It has b.p. 215°–219°; 88°–89°/8 mm., sp.gr. 0·9871 at 20°, n_D 1·45929 at 19°, and when saponified forms *santenol* $C_9H_{16}O$, b.p. 195°–198°, probably identical with π-norborneol. After distillation, santenol forms a solid which when recrystallised forms clear tablets or prisms, m.p. 97°–98°. Its *phenyl urethane* derivative has m.p. 61°–62°; when oxidised with chromic acid, santenol yields a *ketone*, m.p. 58°–59°, the *semicarbazone* of which has m.p. 225°–226° (Aschan, *l.c.*).

Santene glycol $C_9H_{14}(OH)_2$ is formed by dissolving santene in acetone, adding a little water and some powdered potassium permanganate, the whole is then distilled in steam and the distillate extracted with ether. It has m.p. 193°, b.p. 135°/10 mm., and when distilled with sulphuric acid yields a *ketone* $C_9H_{14}O$, b.p. 76°–80°/10 mm. (Semmler and Bartelt, *l.c.* 868).

Santene hydrochloride $C_9H_{15}Cl$, m.p. 80°–81°, is formed by passing hydrochloric acid gas in a cold ethereal solution of santene (Müller, *l.c.*; Aschan, *l.c.*).

Santene tribromide $C_9H_{13}Br_3$, m.p. 62°–63°, is obtained by treating a chloroform solution of santene with bromine (Soden and Müller, Chem. and Druggist, 1900, 57, 282).

Santene nitrosochloride $C_9H_{14}NOCl$, m.p. 109°–110°, is of a blue colour and passes into a white modification after a few hours. On heating to 80°–90° the latter again becomes coloured and has then m.p. 110°–111° (Müller, *l.c.*; Aschan, *l.c.*).

Santene nitrosite, m.p. 124°–125°, has also been prepared (Müller, *l.c.*; Aschan, *l.c.*).

SANTONICA. *Wormseed.* (*Semen-contra*, Fr.; *Wurmsamen*, Ger.) The so-called wormseed consists of the minute unexpanded flower-heads of *Artemisia maritima*, variety *Stechmanniana* (Besser) (*v.* Bentl. a. Trim. 157). The species is widely distributed throughout Europe and Asia; but the variety which yields the more esteemed Levant wormseed of commerce is for the most part confined to southern Russia and Turkestan, especially the district of the lower Volga. Thence the drug enters European markets by way of Nijni Novgorod. The santonica shrub emits a marked camphoraceous odour, which is distinctly perceived in the drug itself when rubbed. The taste is bitter and aromatic (*cf.* Flückiger, Pharm. J. [iii.] 17, 449).

Santonica is used in medicine almost exclusively for its powerful anthelmintic property in the case of the round lumbricoid worm *Ascaris lumbricoides;* but for this purpose its chief active constituent, santonin, has quite superseded the drug itself. When santonin or santonica has been administered the urine assumes a saffron-yellow colour, changed to violet by alkalis, and in many cases the field of vision is suffused with a yellow hue. König finds that the visual power of recognising the ulterior portion of the blue and the entire extent of the violet of the solar spectrum is entirely abolished for the time being, whilst the point of neutrality is situated at the rare length of 573, this being the exact complementary point of the suppressed violet. König infers that the visual phenomena, occasioned by the ingestion of sodium santoninate, do not constitute actual violet blindness, the retina or optic nerve being affected, but that the rays of violet light are, during the santoninic toxical condition, simply absorbed by certain of the media of the eye, which have been abnormally, and, of course, only temporarily, affected by the drug (J. Soc. Chem. Ind., 1889, 566).

The well-known crystalline compound *santonin*, $C_{15}H_{18}O_3$, was discovered in santonica by Kahler in 1830 (Brandes Arch. 34, 318; 35, 216), and independently obtained immediately afterwards by Alms (Brandes Arch. 34, 319; 39, 190). It was further studied by Trommsdorff (Annalen, 11, 190) and by Heldt (*ibid.* 63, 10); also by Oberdörffer (Brandes Arch. 35, 319), Guillemette (J. Pharm. Chim. 26, 152), Roder (Jahrb. pr. Pharm. 6, 45), Miahle and Calloud (J. Pharm. Chim. [ii.] 4, 387), and Cerutti (Arch. Pharm. [ii.] 52, 148). To obtain it the method adopted by the British Pharmacopœia of 1885 may be employed. This is essentially the process of Calloud (J. Pharm. Chim. [ii.] 15, 106). The drug is extracted by digestion with lime and water, and from this solution, after suitable concentration and acidification, the santonin in an impure form slowly precipitates. It has then to be purified by washing with water and dilute ammonia, and by treatment with animal charcoal, and finally, it is dissolved in alcohol and crystallised from that solvent. The crystallisation has to be effected in a dark place, otherwise the product is converted by the actinic rays into a yellow compound, which, at least in those cases where the alcohol is not free from water, is the ethyl ether of a new dibasic acid *photosantonic acid* $C_{15}H_{22}O_5$ (Sestini, Gazz. chim. ital. 6, 357). The yield of santonin varies from 1 to 2 p.c. For the preparation of santonin, see also Busch (J. pr. Chem. [ii.] 35, 322) and Cech (Dingl. poly. J. 253, 474), and for detection and estimation of santonin, Manseau (Chem. Zentr. 1891, ii. 733).

Methods which are modifications of the process just described are also employed in the valuation of specimens of the drug by Dragendorff (Arch. Pharm. 1878, 306) and Flückiger and Ehlinger (*ibid.* [iii.] 24, 1). The following process is given by Flückiger and Ehlinger:—5 parts of wormseed and 1 part of milk of lime are boiled for two hours in a considerable quantity of dilute alcohol, and the liquid poured off after cooling; this treatment is repeated twice, the extracts are mixed, and the alcohol removed by distillation. The residual liquid is then saturated in the cold with carbon dioxide, the mixture, after standing some hours, filtered, and the filtrate evaporated to dryness. The residue is triturated with animal charcoal and alcohol (sp.gr. 0·935), and the paste mixed with more alcohol is heated to boiling. The whole is then thrown on a filter, the residue washed with hot alcohol, and the filtrate concentrated by evaporation, when, after standing for some hours, the santonin separates in crystals and may be dried and weighed (Flückiger, Pharm. J. [iii.] 17, 449).

Santonin crystallises from water in flattened hexagonal prisms and from ether in rhombic plates. It melts at 170° (Schmidt, Zeitsch. Chem. 1865, 320; Leroy, Rep. Pharm. 1878, 104), and when heated to a higher temperature in small quantities it may be sublimed. It is nearly insoluble in water; but is soluble in ether, and more so in alcohol and chloroform (*cf.* Trommsdorff; Schlimpert, Arch. Pharm. [ii.] 100, 151). The alcoholic solution is strongly lævorotatory (Buignet, J. Pharm. Chim. [iii.] 40, 252; Hesse, Annalen, 176, 125). If a small fragment of santonin be dissolved in cold sulphuric acid and a drop of ferric chloride solution be added, there is developed a beautiful crimson colour which passes over to purple and violet (Lindo, Chem. News, 36, 222; Knopp, Dingl. poly. J. 268, 42). A crimson colour is also obtained when santonin is treated with alcoholic potash (Heldt). When heated with dilute acids sugar is not formed (Schmidt, Zeitsch. Chem. [ii.] 1, 212).

Halogen derivatives were obtained from santonin by Heldt (Annalen, 63, 32) and by Sestini (Ber. 5, 202), and it is shown to form definite addition compounds with metallic oxides. *Monochlorosantonin* $C_{15}H_{17}ClO_3$, *dichlorosantonin* $C_{15}H_{16}Cl_2O_3$, and *trichlorosantonin* $C_{15}H_{15}Cl_3O_3$ were prepared, and metallic compounds having the general formula

$$C_{15}H_{18}O_3,M'_2O.$$

The compound with sodium consists of large rhombic prisms. These metallic compounds were proved by Hesse (Ber. 6, 1280) to be combinations of a new acid of which santonin is the anhydride, and not to be salts of santonin, as was at first supposed. This new *santoninic acid* $C_{15}H_{20}O_4$ is obtained when the sodium compound of Heldt is treated with a mineral acid. Its salts, the santoninates, are formed by the addition of a molecule of a metallic oxide to a molecule of the anhydride, santonin. The free acid may also be easily reconverted into santonin by the removal of the elements of water. This is accomplished by simply heating it to 120°, or by treatment with concentrated sulphuric acid.

Santoninic acid consists of colourless granular crystals which are unaffected by sunlight.

By the prolonged application of heat and by the action of reagents a large number of isomerides of santoninic acid and its anhydride, santonin, and other related compounds, have been brought to light chiefly by Canizzaro and his pupils. A short account of the modern views of the constitution of santonin and some of its derivatives—the outcome of these researches—is given by Wedekind (Arch. Pharm. 244, 623). For the physiological action of santonin derivatives, many of which have been used in medicine, see Coppolo (Chem. Soc. Abstr. 54, 310; Wedekind, Zeitsch. physiol. Chem. 43, 240).

Santonica contains, besides santonin and the substances found in all plants, certain volatile constituents. When distilled with steam 1 to 2 p.c. of a *volatile oil* passes over, which contains α-pinene, terpinene, terpineol, and terpinenol, and a sesquiterpene (b.p. 250° approx.) (Schimmel, Semi-Annual Rep. 1908; *cf.* Schindel-Meiser, Apoth. Zeit. 22, 876). The last mother-liquors in the technical treatment of the seed of *Artemisia maritima* contain *artemisin* $C_{15}H_{18}O_4$. It is freed from santonin by recrystallisation from chloroform, being deposited in combination with 1 molecule of that solvent. Artemisin melts at 200°, gradually turns yellow in the air, and is more readily soluble in water or dilute alcohol than santonin (Merck, Chem. Zentr. 1895, i. 436). A. S.

SANTONIN, SANTONINIC ACID *v.* SANTONICA.

SAPAN- or SAPPANWOOD *v.* BRAZILWOOD.

SAPONARIA OFFICINALIS (Linn.). The epidermal cells of the leaves of certain flowering plants contain, dissolved in their cell sap, a substance which is coloured blue by iodine. The colour disappears on warming and returns on cooling, as is the case with starch. On this account the compound was regarded as an amorphous variety of starch by Sanio, its discoverer (Botanische Zeitung. 1857, 15, 420). Schenck (*ibid.* 1857, 15, 497, 455) doubted whether this substance was identical with starch, and the correctness of this view was confirmed by Nägeli (Beiträge. zur wissensch. Botanik. 1860, 2, 187). For the chemical examination of this substance the dried shoots of the *Saponaria officinalis* were selected by Barger (Chem. Soc. Trans. 1906, 89, 1210) as the raw material, because this plant is relatively rich in the compound, and is grown on the Continent for pharmaceutical purposes, so that large quantities are easily obtainable.

Saponarin $C_{21}H_{24}O_{12},2H_2O$. The material was extracted with from 10 to 20 times its weight of water for half an hour, and the operation repeated several times. The extracts, strained through linen and concentrated to a quarter their volume, were acidified with acetic acid and left to stand for several weeks. The grey deposit which had then separated was dissolved in hot 1 p.c. sodium carbonate solution (1 litre per kilo. of dry leaves), and after addition of acetic acid was treated with lead acetate, in order to precipitate gums and other impurities. On standing for several weeks the clear liquid deposited crude saponarin, which, however, still contained 30 p.c. of impurity.

The crude saponarin was dissolved in boiling pyridine, the dark brown solution was filtered and evaporated in a vacuum on the water bath. The residual syrup dissolved in hot water was diluted and on standing deposited the substance in microscopic needles.

Saponarin dried in air is a white powder, but after being dried in a vacuum becomes pale yellow, and is soluble in dilute alkaline solutions with an intense yellow colour. When heated slowly it melts and decomposes at 231°–232°, but if the bath is previously heated to 230°, the melting-point is 236°.

On acidifying an alkaline solution, and on diluting a solution in concentrated acids with water, the glucoside is not immediately precipitated if the solution is dilute. This power of remaining in a state of pseudo solution is characteristic of saponarin, and in this condition it gives with iodine in potassium iodide the blue or violet colouration which led to its discovery. This colouration disappears on warming, but returns again on cooling. Saponarin gives with sulphuric acid a blue fluorescent solution.

Ennea-acetyl saponarin $C_{21}H_{15}O_{12}(C_2H_3O)_9$, microscopic curved needles, melts at 183°–185°. It does not give a blue colouration with iodine. When saponarin is boiled with dilute mineral acids, it is slowly hydrolysed according to the equation

$$C_{21}H_{24}O_{12}+H_2O=C_{15}H_{14}O_7+C_6H_{12}O_6$$

with formation of glucose, *saponaretin* and a small quantity of *vitexin* identical with that obtained by Perkin (Chem. Soc. Trans. 1898, 73, 1030) from the *Vitex littoralis* (A. Cunn). According to Barger, vitexin forms pale yellow glistening plates, m.p. 260°, whereas it is described by Perkin as canary yellow needles, m.p. 264°–265°. Molecular weight determinations carried out by the microscopic method (Barger, Chem. Soc. Trans. 1904, 85, 286; 1905, 87, 1756) indicate that the original formula $C_{15}H_{14}O_7$ assigned by Perkin to vitexin is correct (*l.c.*), rather than the second suggested formula of this latter author $C_{21}H_{20}O_{10}$.

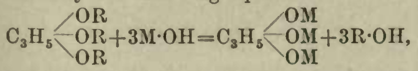
Saponaretin $C_{15}H_{14}O_7$?, the chief product of the hydrolysis of saponarin with dilute acid consists of a light yellow amorphous powder, extremely soluble in alcohol, though in other respects it closely resembles vitexin. It may be that saponaretin is identical with Perkin's homovitexin (*l.c.*), which in the case of the *Vitex littoralis* appears to be the minor product of the hydrolysis of the glucoside there present.
A. G. P.

SAPONARIN *v.* SAPONARIA OFFICINALIS (Linn.).

SAPONIFICATION. The chemical change which takes place on boiling fats with strong bases, and which results in the formation of glycerol and of salts of the higher fatty acids, has been termed 'saponification.' In a wider sense, however, every chemical process by which oils and fats are resolved into their proximate constituents—glycerol and fatty acids, is called saponification, even if no bases be used to effect the reaction.

The term 'saponification' is almost exclusively used in practice, its synonym 'hydrolysis' being confined to papers of a scientific character.

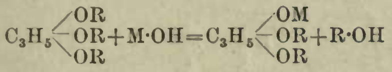
The chemical change which oils and fats undergo on being hydrolysed or saponified is expressed by the following equation :—

(1) 

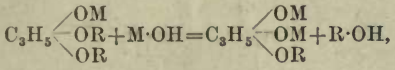
$$C_3H_5{<}\begin{matrix}OR\\OR\\OR\end{matrix}+3M\cdot OH=C_3H_5{<}\begin{matrix}OM\\OM\\OM\end{matrix}+3R\cdot OH,$$

where R denotes the radicle of any fatty acid, and M stands for hydrogen or a monovalent metal. (In the case of a bivalent metal, equation (1) must be replaced by equation (3*a*).)

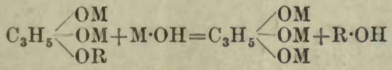
In the light of experiments made by Geitel and by Lewkowitsch, this equation must be considered as summarising the following three equations :—

(1*a*) 

$$C_3H_5{<}\begin{matrix}OR\\OR\\OR\end{matrix}+M\cdot OH=C_3H_5{<}\begin{matrix}OM\\OR\\OR\end{matrix}+R\cdot OH$$

(1*b*) 

$$C_3H_5{<}\begin{matrix}OM\\OR\\OR\end{matrix}+M\cdot OH=C_3H_5{<}\begin{matrix}OM\\OM\\OR\end{matrix}+R\cdot OH,$$

(1*c*) 

$$C_3H_5{<}\begin{matrix}OM\\OM\\OR\end{matrix}+M\cdot OH=C_3H_5{<}\begin{matrix}OM\\OM\\OM\end{matrix}+R\cdot OH$$

These equations express the fact that hydrolysis (saponification) takes place in three stages, the triglyceride passing through the diglyceride and the monoglyceride to the products of complete hydrolysis.

On carrying out 'hydrolysis' or 'saponification' on a practical scale, we cannot expect these three stages to take place consecutively, in distinct succession; or in other words, we cannot expect to find that the whole mass of triglycerides is at first hydrolysed exclusively to diglycerides (as indicated by the equation 1*a*), that the diglycerides are then broken down to monoglycerides (as shown by the equation 1*b*), and that finally the monoglycerides so formed are converted into glycerol and free fatty acid (1*c*). We shall rather find that the three phases, which are expressed by the above three equations, take place concurrently, so that at one and the same time a molecule of diglyceride may be broken down to monoglyceride and fatty acid, or a molecule of monoglyceride to glycerol and fatty acid, whilst a molecule of triglyceride is still intact, or is passing through the first phase. Therefore, on bringing about very rapid hydrolysis we shall not always be able to observe experimentally the intermediate transitory phases. If, however, hydrolysis or saponification be effected somewhat slowly, we are able to find in the partially saponified mass: (1) unsaponified triglyceride, (2) diglyceride, (3) monoglyceride, (4) glycerol, and (5) free fatty acid.

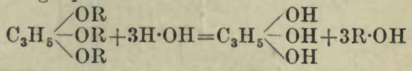
This has been verified to some extent by experiments of Geitel and especially by those of Lewkowitsch (J. Soc. Chem. Ind. 1898, 1107; Chem. Soc. Proc. 1899, 190; Ber. 1900, 89).

Reasoning by analogy, hydrolysis by means of sulphuric acid should also take place in stages. Direct experimental proof may be found in the observation made by Gruen and Theimer (Ber. 1907, 1801) (*cp.* also B. W. van Eldik Thieme, Koningkl. Akad. van Wetensch. Amsterdam, 1908, 855), that on hydrolysing distearo-α-chlorohydrin with 98 p.c. sulphuric acid there were obtained, in addition to still unchanged distearochlorohydrin, the following products: monostearochlorohydrin, monochlorohydrin, and stearic acid. These products of hydrolysis thus represent the three stages of diglyceride, monoglyceride, and free fatty acid. Similarly, glyceryl trinitrate is hydrolysed by a 70 p.c. sulphuric acid to glycerol dinitrate; and glyceryl dinitrate in its turn to mononitrate and glycerol.

In full agreement with the foregoing is the evidence afforded by the synthesis of triglycerides, as it is possible to build them up from glycerol and fatty acid to monoglyceride, from the monoglyceride to diglyceride, and from the diglyceride to triglyceride (Berthelot).

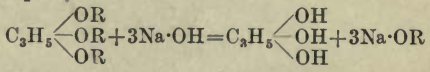
The occurrence of dierucin (in old rape oil), for a long time looked upon as an exceptional phenomenon, is now satisfactorily explained, and the presence of mono- and diglycerides in rancid fats becomes very probable. This is well illustrated by the changes olive oil undergoes in stored olives (*see* Olive oil).

Since in the absence of water no hydrolysis can take place, water must be considered as the hydrolysing agent, whether it be employed alone, or whether its action be assisted by catalytic agents, such as acids or ferments. In these cases the reaction is expressed by the following equation :—

(2) 

$$C_3H_5{<}\begin{matrix}OR\\OR\\OR\end{matrix}+3H\cdot OH=C_3H_5{<}\begin{matrix}OH\\OH\\OH\end{matrix}+3R\cdot OH$$

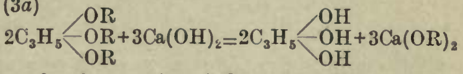
If bases be chosen as catalysts (catalysers) a further chemical reaction takes place, viz. the combination of the base with the liberated fatty acids. Thus if in equation (1) M be a monovalent metal, *e.g.* sodium, the final products will be glycerol and soda soap, as expressed by the equation—

(3) 

$$C_3H_5{<}\begin{matrix}OR\\OR\\OR\end{matrix}+3Na\cdot OH=C_3H_5{<}\begin{matrix}OH\\OH\\OH\end{matrix}+3Na\cdot OR$$

If divalent metals, such as calcium, be used then equation (3) would be replaced by (3*a*)—

(3*a*)



$$2C_3H_5{<}\begin{matrix}OR\\OR\\OR\end{matrix}+3Ca(OH)_2=2C_3H_5{<}\begin{matrix}OH\\OH\\OH\end{matrix}+3Ca(OR)_2$$

On the reactions indicated by the foregoing equations are based the processes which are carried out on the largest scale in the fat industries, especially in the operations involving the manufacture of fatty acids and of soaps. In this article, prominence must be given to the practical side of saponification; for the theoretical aspect of this question the reader must be referred to Lewkowitsch, Chem. Technology, i. chap. 2.

Saponification without the Assistance of Catalysts.

Aqueous saponification. The realisation of the fundamental equation of fat hydrolysis

$$C_3H_5(OR)_3+3H\cdot OH=C_3H_5(OH)_3+3R\cdot OH$$

suggests itself to the candle-maker as the ideal process. The first attempt to work such a process on an industrial scale was made by R. A. Tilghmann, whose method consisted in forcing an emulsion of fat and water through a coiled iron tube, heated in a furnace to a temperature of about 330°. This process was, however, soon abandoned on account of the fact that hydrolysis was incomplete and considerable quantities of fatty matter were destroyed. More successful have been the modern processes of hydrolysis by means of steam at a pressure of 15 atmospheres (equivalent to about 220 lbs. per square in.) and corresponding to a temperature of about 200°. An apparatus which the author saw working on a practical scale in a Paris candleworks is the Hughes apparatus shown in Fig. 1.

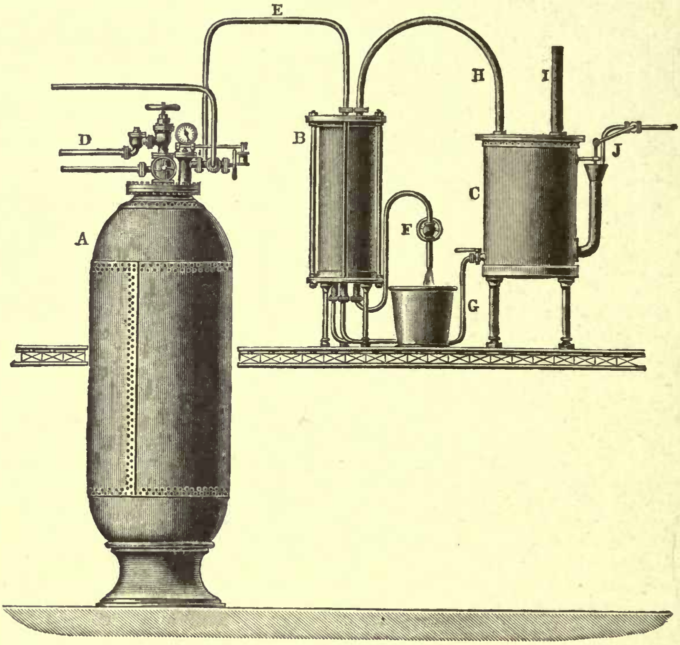


Fig. 1.

The fat is charged into the autoclave A, about 30 p.c. of water is added, and steam, generated in a multitubular boiler at a pressure sufficiently high to keep up a working pressure of 15 atmospheres in the apparatus, is sent into the autoclave. The steam is divided into streamlets by a distributor similar to the one shown in Fig. 3. In order to provide additional security against explosion (beyond that afforded by the safety valve) and in order to agitate the mass thoroughly, a small amount of steam is allowed to escape continuously through the pipe E, which thus serves as an additional safety valve. The escaping steam is utilised for the concentration of a glycerin solution charged (through pipe G) into vessel B, the condensed water escaping through valve F, which acts as a kind of steam-trap. The steam evolved from the glycerin solution in B serves to pre-heat a dilute glycerin solution fed into vessel C at J. In consequence of the high temperature employed, the fatty material becomes seriously discoloured, so that the fatty acids must be chiefly worked up by the 'mixed process' (see below). Moreover, since the hydrolysis of the fat does not reach so high a percentage as is the case in the processes described under (2), a small proportion of lime, about 1 p.c., is usually added to the mass in the autoclave. Hence, practically speaking, this method approaches very nearly those described under *Saponification with the Aid of Bases under Pressure.*

Saponification with the Aid of Catalysts.

It has been indicated above that catalytic agents are capable of accelerating the process of hydrolysis, in other words, that a small amount of such an agent is capable of producing hydrolysis at a more rapid rate and at a lower temperature than is employed in the case of aqueous saponification under pressure. If bases are used as accelerating agents it would therefore follow that it should not be imperative that the bases be present in at least molecular proportion to the quantity of fatty acids that will result on complete hydrolysis. The greater the amount of the bases present the more rapidly should the resolution of the glycerides into their proximate components take place, and the greater should be the amount of salts of the fatty acids formed. But a deficiency of the bases necessary to neutralise all the fatty acids obtainable by complete hydrolysis, should not preclude the completion of hydrolysis.

Since the velocity of saponification stands in direct ratio to the quantity of the bases, then, in the presence of an excess of bases, it should be possible to lower the temperature and shorten the time required for effecting practically complete hydrolysis. These views are confirmed by practice in the several modifications of the technical process of saponifying by means of lime.

1. *Saponification by means of lime in the open vat.* The amount of caustic lime—CaO—required for a triglyceride having the mean molecular weight 860, is according to equation

(3*a*) 9·7 p.c., but even prolonged boiling with steam in an open vessel with that proportion of lime will not lead to complete saponification. Unless the proportion of caustic lime be raised to 12–14 p.c., the hydrolysis of the triglyceride cannot be brought to an end in an open vessel, *i.e.* at a temperature of from 100° to 105°.

The technical process based on the saponification of oils and fats by means of 12 to 14 p.c. of lime, and leading to the conversion of the total fatty acids into lime soaps, is due to De Milly. The fat is churned up with water in an open lead-lined vat by means of live steam sent into the emulsion through an open coil; whilst the mass is kept in ebullition, caustic lime previously slaked and made into a thin cream is gradually introduced. The boiling is maintained until the saponification is complete; this is readily recognised by the lime soap separating from the water in a curdy form. The glycerin water—'sweet water'—is then run off; the still soft lime soap is washed to remove occluded glycerol, and is then decomposed with sulphuric acid. In the older methods the lime soap was allowed to cool, when it settled as a hard mass—'rock'—from which the supernatant glycerin solution was run off. This hard lime soap was then washed, reduced to powder by grinding, and decomposed with sulphuric acid, when the calcium was precipitated as sulphate, whilst the liberated fatty acids rose to the top as a clear oily layer. The fatty acids and the glycerin—'sweet water'—are worked up for candle material (*see* below) and crude glycerin (*see* GLYCERIN).

The large amount of lime (and consequently the large amount of sulphuric acid) required in the process renders it costly, so that it has been largely superseded by methods of saponification under pressure (*see* below).

A modification of this method has been worked out during latter years by Krebitz. The saponification with lime is in principle the same as described above, with this difference, however, that the fat is not boiled with the lime until separation of the lime soap takes place, but that the water is brought into a state of complete emulsion with the oil or fat at a temperature not exceeding 100°. This emulsion is then allowed to stand overnight, when saponification takes place spontaneously, and a softish mass results which occludes the water introduced with the lime, and the glycerol formed. This mass does not offer as much difficulty in grinding as the 'rock' does. The ground lime-powder is then washed free from glycerol, when the lime soap is ready for further treatment. This process is unsuitable for candle-works. It has been introduced in some small continental soap works working up low-class bone fats, where the ground lime soap is converted into soda soap by double decomposition with sodium carbonate solution (*see* SOAP).

The process of saponification by means of lime in the open vat has, at least so far as *candle making material* is concerned, become altogether obsolete, since a reduction of the amount of bases and acids has become imperative with a view to reduction of manufacturing costs.

2. *Saponification with the aid of bases under pressure.* If the lime be considered a catalytic agent then it should be possible, in correspondence with the views expressed above, to reduce the proportion of lime. This is actually done by carrying out the hydrolysis by means of lime in an autoclave under pressure. Under these conditions the proportion of caustic lime can be reduced gradually until, at a pressure of 12 atmospheres (corresponding to a temperature of 190°), even 1 p.c. of lime suffices for practically complete hydrolysis. Although the glyceride is, practically speaking, completely hydrolysed, only so much of the fatty acid is neutralised by lime—*i.e.* converted into lime soap—as is chemically equivalent to the quantity of lime employed (*see* above).

The practice of the candle industry has, however, shown that at such high pressure the fatty acids become much discoloured; hence it has been found more advantageous to reduce the temperature whereby an increase of the amount of catalyst required becomes necessary.

In the modern practice of *candle-works*, autoclaves are therefore worked at a pressure of about 8 atmospheres (=120 lbs. per sq. in.). At this pressure, when employing about 3 p.c. of lime, the fat is practically completely hydrolysed. The autoclaves in use are illustrated by Figs. 2 and 3. That shown in Fig. 2 consists of a cylindrical vessel made of copper, strong enough to withstand a working pressure of 8 atmospheres, and provided with an internal steam pipe which reaches the bottom of the vessel. In Fig. 2 the steam leaves at the bottom of the serrated cone, and is thus divided

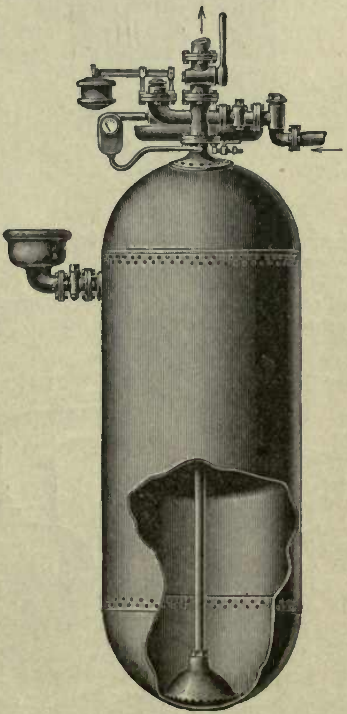


FIG. 2.

into a number of streamlets which churn the mixture of fat and water into a thorough emulsion. The water and fat, in the proportion of 1 to 3, or 1 to 4, as also the milk of lime, are fed through the funnel-shaped vessel at the side of the autoclave.

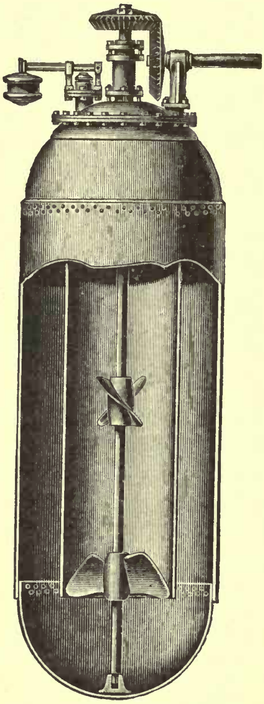


Fig. 3.

When the autoclave is charged, steam is turned on and the vessel is kept at a pressure of 8 atmospheres for about 8 to 10 hours.

The following table illustrates the hydrolysis of tallow saponified in an autoclave with 3 p.c. of lime at a pressure of 8 atmospheres.

					Free fatty acids, per cent.
Sample taken	after the	1st	hour	contained	38·55
,,	,,	2nd	,,	,,	77·40
,,	,,	3rd	,,	,,	83·9
,,	,,	4th	,,	,,	87·5
,,	,,	5th	,,	,,	88·6
,,	,,	6th	,,	,,	89·3
,,	,,	7th	,,	,,	93·0
,,	,,	8th	,,	,,	97·5
,,	,,	9th	,,	,,	98·1
,,	,,	10th	,,	,,	98·6

In the form of autoclave shown in Fig. 3, the agitation, effected by steam, is assisted by a mechanical stirring arrangement.

A horizontal form of autoclave fitted with a stirring arrangement of a different kind is illustrated by Fig. 4.

Since cylindrical autoclaves if not sufficiently strong are liable to be bulged out by the high pressure, they would at last, if the bulging took place progressively in a regular manner, assume the shape of a sphere. Hence spherical autoclaves (first suggested by L. Bottaro of Genoa) are also in vogue. An autoclave of this kind, provided with a stirring arrangement, is shown in Fig. 5.

In the processes considered here the hydrolysis reaches as high a figure as 98 to 99 p.c. If the temperature, time and amount of reagent be reduced the hydrolysis may not reach so high a degree and may only amount to 96 to 97 p.c.

For the purposes of the candle industry, such discolouration as the fatty acids unavoidably undergo in this process is of little account, as the colouring bodies can be easily removed by subsequent treatment. Since, however, attempts have been made to apply this process of hydrolysis to fats intended for soap making (*see* Soap), it was found necessary still further to reduce the temperature, and the autoclaves are therefore worked for this purpose at a pressure of 5 to 6 atmospheres only. This feature (intensified by an attempt to reduce the proportion of bases) leads to a reduction of the proportion of fat undergoing hydrolysis; hence, in the practice of preparing fatty acids for purposes of soap-making no higher amount of hydrolysis than about 80 p.c. is reached. Even at this pressure, serious discolouration of the fatty acids takes place (*see* Soap). The technical

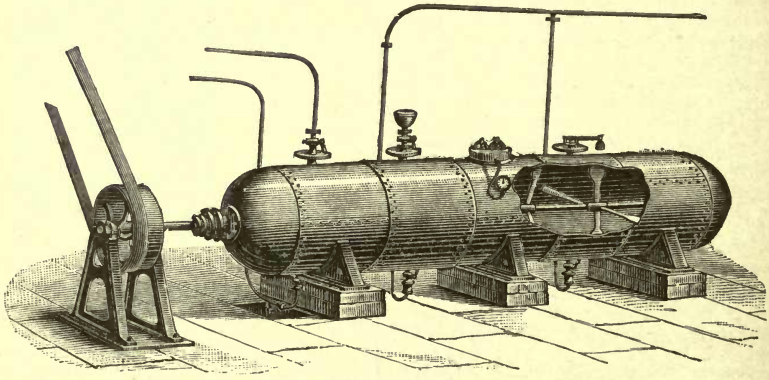


Fig. 4.

operation is conducted practically in the same manner as described under *Aqueous saponification.*

When the saponification is deemed complete, the saponified mass is allowed to stand in the autoclave until it has separated into two layers: glycerin water—'sweet water'—and an upper layer of fatty acids, containing as much lime soap as corresponds with the lime introduced into the autoclave. These two layers are either pumped separately into store vats or the whole mass may be pumped into a settling vat, where the separation into two layers takes place. The further working up of the glycerin solution into 'crude saponification glycerin' has been described under Glycerin. The fatty layer is boiled up with steam, and sufficient sulphuric acid is added to decompose the lime soap. On allowing to stand, most of the calcium sulphate separates out at the bottom of the aqueous layer, whereas the fatty acids form a clear oily layer on the top. They are washed carefully with dilute acid to remove the last traces of lime. Some manufacturers precipitate the lime in the last stages as oxalate.

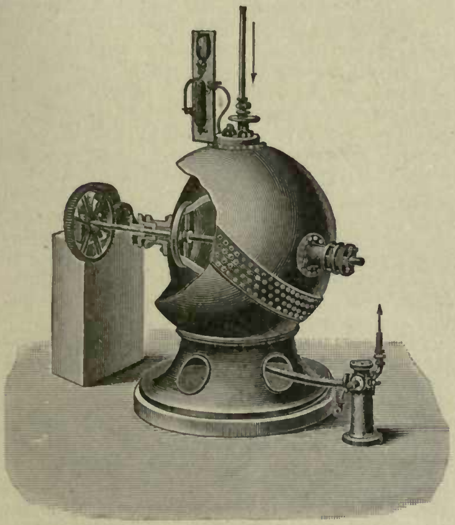


Fig. 5.

In place of lime, magnesia and zinc oxide (to which latter zinc dust is also added), are employed as 'accelerators.' The advantage offered by magnesia and zinc oxide consist in the fact that they do not yield a precipitate on decomposing the autoclaved fatty matter with sulphuric acid. This advantage is, however, counterbalanced by the fact that hydrolysis is not so readily effected by means of magnesia, at any rate in the case of tallow and palm oil, as by means of lime. Experience gained on a large scale has shown that tallow, autoclaved with 3 p.c. of magnesia under the same conditions as with 3 p.c. of lime, is hydrolysed only to the extent of about 96 p.c. In order to reach as good a result as is obtained by means of lime, the working pressure or (and) the length of time must be increased. This is borne out by the following table:—

Saponification of Shea Butter with 3 per cent. of Magnesia at a Pressure of 9 Atmospheres.

			Free fatty acids, per cent.	
Sample taken after the	1st hour	contained	61·4	63·2
,, ,,	2nd ,,	,,	80·2	81·9
,, ,,	3rd ,,	,,	90·2	90·1
,, ,,	4th ,,	,,	91·1	94·8
,, ,,	5th ,,	,,	95·4	95·7
,, ,,	6th ,,	,,	95·5	97·1
,, ,,	7th ,,	,,	96·6	97·1
,, ,,	8th ,,	,,	98·1	98·0

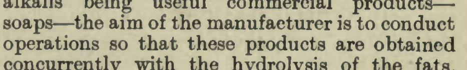
The pressure being higher than in the case of lime, discolouration of the fatty acids takes place to a somewhat greater extent, and the resulting 'sweet water' is more dilute. The chief disadvantage of magnesia lies, however, in the fact that it frequently gives emulsions, which are very troublesome, as they do not separate even after prolonged standing and, as pointed out already, that the saponification is less complete.

Zinc oxide does not offer these disadvantages, but its higher cost outweighs the benefit derived from its use. A small percentage of zinc oxide or zinc dust is, however, frequently used conjointly with lime, as the discolouration of the fatty acids is thereby somewhat diminished.

3. *Saponification by means of caustic alkalis.* There can be no doubt that under pressure, complete hydrolysis would be brought about by an amount of caustic alkali insufficient to neutralise all the fatty acids formed. On a large scale, for obvious reasons, such a process is not employed. The compounds resulting from the combination of fatty acids and caustic alkalis being useful commercial products—soaps—the aim of the manufacturer is to conduct operations so that these products are obtained concurrently with the hydrolysis of the fats. Hence, on a commercial scale, oils and fats are boiled in open vessels with a solution of caustic alkalis, containing not only sufficient alkali to neutralise all the fatty acids obtainable on hydrolysing the glycerides, but also an excess, whereby the time required for the completion of the reaction is shortened. Indeed, this excess of alkali is required in order to carry out the reaction in the shortest possible time (*see* Soap).

The laboratory method of saponifying fats by means of alcoholic caustic potash or caustic soda (*see* Oils, Fixed, and Fats) need not be considered as differing, theoretically, from hydrolysis in aqueous solutions, if we look upon alcohol as water in which one hydrogen atom is replaced by the group C_2H_5. Ignoring for a moment the alkali, hydrolysis would proceed according to the following equation:

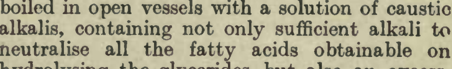
(5)



$$C_3H_5\begin{array}{l}\diagup OR\\ -OR\\ \diagdown OR\end{array}+3H\cdot OC_2H_5=C_3H_5\begin{array}{l}\diagup OH\\ -OH\\ \diagdown OH\end{array}+3R\cdot OC_2H_5$$

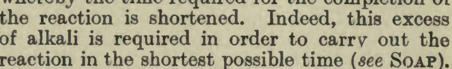
which should, again, be looked upon as a summary of the following three equations:

(5*a*)



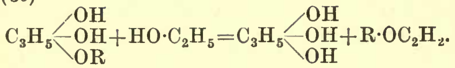
$$C_3H_5\begin{array}{l}\diagup OR\\ -OR\\ \diagdown OR\end{array}+HO\cdot C_2H_5=C_3H_5\begin{array}{l}\diagup OH\\ -OR\\ \diagdown OR\end{array}+R\cdot OC_2H_5;$$

(5*b*)



$$C_3H_5\begin{array}{l}\diagup OH\\ -OR\\ \diagdown OR\end{array}+HO\cdot C_2H_5=C_3H_5\begin{array}{l}\diagup OH\\ -OH\\ \diagdown OR\end{array}+R\cdot OC_2H_5;$$

(5*c*)



$$C_3H_5\begin{cases}OH\\OH\\OR\end{cases}+HO\cdot C_2H_5=C_3H_5\begin{cases}OH\\OH\\OH\end{cases}+R\cdot OC_2H_2.$$

The resulting products would be glycerol and the ethylic esters of the fatty acids. Although the feasibility of those reactions had not been tested experimentally, the author (J. Soc. Chem. Ind. 1903, 595) had expressed the opinion that with anhydrous materials and under high pressure, especially if assisted by a suitable catalyst, the reaction would very likely proceed a long way in the direction indicated by the equation (5).

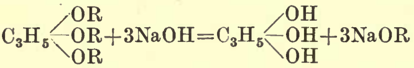
In the absence of water the chemical change cannot proceed beyond the formation of ethyl-esters. But if the alcohol contain water, the ethyl-esters in their turn are hydrolysed by the water to some extent. Complete hydrolysis, such as indicated by the following equation

$$(6)\ 3C_2H_5\cdot OR+3H\cdot OH=3R\cdot OH+3C_2H_5\cdot OH,$$

cannot result, since an equilibrium between ester, water, and free fatty acids would soon be established. The reaction thus arrested will, however, proceed if alkali be present to neutralise the free acid formed. Since in laboratory operations caustic alkali is added to the alcohol in quantity greater than that which is chemically equivalent to the fatty acids, the fatty acids formed (equation 6) will be immediately neutralised, as is illustrated by the following equation:

$$(7)\ 3R\cdot OH+3Na\cdot OH=3Na\cdot OR+3H\cdot OH$$

Hence, the chemical change represented by equation (6) will become complete. By adding the three equations (5, 6, and 7), we obtain as the final result



$$C_3H_5\begin{cases}OR\\OR\\OR\end{cases}+3NaOH=C_3H_5\begin{cases}OH\\OH\\OH\end{cases}+3NaOR$$

which is identical with the above-given equation (3).

For further explanation dealing with the mechanism of saponification in alcoholic solution and the action of sodium ethylate, *cp.* Lewkowitsch, Chem. Technology, i. 80 ff.

4. *Saponification by means of ammonia.* Ammonia is also capable of acting as an accelerating agent in the hydrolysis of oils and fats, and has therefore been frequently suggested as a saponifying agent. The properties of ammonia render it imperative to carry out the hydrolysis under pressure, and several special autoclaves have been patented for this purpose. None of these suggestions has found practical application. Barbé, Garelli, and de Paoli claim that in their process (protected by French Patent 372431 and 1st Add. No. 9255), the total amount of ammonia is recovered by treating the ammonia soap formed in a current of steam.

5. *Saponification by means of acids.* Just as in the case of many chemical reactions acids act as catalysts, it is possible to employ acids as catalytic agents in accelerating the hydrolysis effected by water.

(a) *Saponification by means of hydrochloric acid.* The author (J. Soc. Chem. Ind. 1903, 67) has shown that oils and fats can be hydrolysed by means of hydrochloric acid, sp.gr. 1·16. As this method has not yet acquired practical importance, it need only be pointed out here that hydrolysis becomes much slower after about 75 p.c. of the neutral fats has been hydrolysed. The fact that under the conditions of the experiments it was very difficult to keep up a thorough intermixture of fat and acidulated water, satisfactorily explains this slowing down of the reaction. It may be safely assumed that provided a thorough intermixture, as in an emulsion, could be brought about, hydrolysis would proceed much more rapidly, for the catalytic action of hydrochloric acid takes place even at the ordinary temperature, provided sufficient length of time be allowed, as has been proved by experiments.

(b) *Saponification by means of concentrated sulphuric acid.* Much better results are obtained by employing as a catalyst *concentrated sulphuric acid,* which seems to act to some extent as an emulsifying agent in the *technical process of hydrolysis by means of concentrated sulphuric acid.* The action of sulphuric acid, first described by Cornett in 1777, consists, in the first instance, in the formation of sulpho-compounds of glycerides, the composition of which has been investigated by Geitel (J. pr. Chem. 1888, 37, 53; *cp.* Lewkowitsch J. Soc. Chem. Ind. 1897, 392).

The technical operation consists in rapidly intermixing fat which has previously been heated to a temperature of 120° or more (and thereby freed from the last traces of moisture) with 4–6 p.c. of concentrated sulphuric acid of 66°–67°Bé. If sulphuric acid of lower strength be used the hydrolysis is not complete (*cp.* Lewkowitsch, Chem. Tech. of Oils, &c., i. 65). With the decrease of the strength of sulphuric acid hydrolysis decreases rapidly; an acid of 60 p.c. SO_4H_2 is no longer capable of effecting hydrolysis on a practical scale. The behaviour of sulphuric acid towards the saturated glycerides is of little practical importance, since sulphonated compounds (of the glycerides as well as of the saturated fatty acids) that are formed are subsequently decomposed, yielding the original saturated acids practically unchanged. With olein, however (less saturated glycerides than olein need not be considered here, as being of no practical importance in the manufacture of 'stearine'), the sulphuric acid forms saturated sulphonated compounds, a small quantity of sulphurous acid being at the same time evolved in consequence of secondary reactions. These sulphonated compounds have the property of being somewhat readily hydrolysed on boiling with water. The chemical change will be referred to below; here it may suffice to state that from 15 to 17 p.c. of oleic acid are converted into solid products, chiefly stearolactone and isomeric solid oleic acids ('isoöleic acid,' *see* OILS, FIXED, AND FATS) with which small quantities of hydroxy acid may be admixed.

The higher the temperature to which the fat has been heated and the larger the percentage of sulphuric acid used, the more copious is the evolution of sulphurous acid and the further will the secondary reactions proceed. In order to reduce the destruction ('carbonising') of organic matter, which necessarily leads to a lower yield of fatty acids, and especially of glycerin, great attention must be paid to the following factors: quantity of sulphuric acid, temperature, and time during which the acid is allowed to act on the fat. In order to ensure the most intimate contact of the fat with the acid within the shortest possible time, various mixing machines are used. Mixing by means of air cannot be recommended, as this leads to deterioration of the material and to appreciable losses. One type of apparatus is shown in Fig. 6. Other devices consist of pulverising the fatty matter by centrifugal force, &c.

(c) *Saponification by means of sulpho-aromatic compounds.* A much more pronounced emulsifying action than that produced by concentrated sulphuric acid is obtained by the sulpho-aromatic compound invented by Twitchell. The reagent employed in this process is obtained by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons. The product obtained in case benzene is chosen as the aromatic hydrocarbon has been described by Twitchell as having the composition $C_6H_4(SO_3H)(C_{18}H_{35}O_2)$. The composition of the reagent as actually supplied to the licensees under the name of 'saponifier' is kept secret. The author does not, therefore, feel justified in making detailed statements as to the manner in which it is prepared for manufacturing purposes beyond pointing out that the aromatic hydrocarbon in the 'saponifier' is naphthalene.

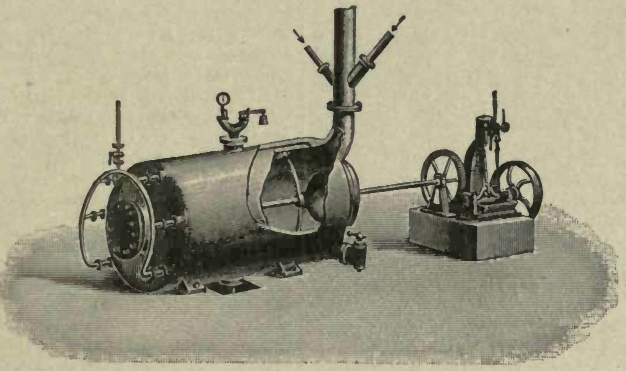


Fig. 6.

The rationale of this process is not yet fully understood. The present author explained the action of the reagent by its power of emulsifying the glycerides and has shown that the same emulsifying action is produced by reagents prepared from anthracene and phenanthrene (*cp.* Lewkowitsch, Chem. Tech. i. 86). The 'Twitchell process' differs most essentially from the 'acid saponification process,' in that oleic acid is not simultaneously converted into solid material; hence the fatty acids obtained by this process have the same composition as those yielded by the autoclave process. This last-mentioned fact would seem to prove that true sulphonated acids have not been formed; moreover, it has been shown above that dilute sulphuric acid does not produce hydrolysis.

It is essential that the fatty material to be treated by this process be freed from impurities, such as lime, iron, as also from foreign organic substances. This is done by boiling the fat with a dilute solution of sulphuric acid. The purified fat is then transferred to wooden vessels furnished with perforated brass coils and provided with well-fitting lids, which allow the steam to escape but prevent free access of air, since the fatty acids formed in this process readily darken on coming into contact with air. In these vessels the fat is mixed with 50 p.c. of its weight of distilled water, 1·5 to 2 p.c. of the reagent are then added, and the whole mass is agitated by open steam passing through the perforated coil. It is essential that the fatty matter contain at the outset a small proportion of free fatty acids, as an entirely neutral fat requires a somewhat lengthy time before hydrolysis commences. This is no doubt due to the fact that the aqueous solution of the reagent requires the presence of fatty acids, in order to produce an emulsion which is essential for the progress of hydrolysis. With neutral fats a somewhat longer time is required to start the hydrolysis, as free fatty acids must be produced first by the boiling with water. But even at best the process requires a considerable time for the practical completion of hydrolysis.

For the purposes of the candle-maker it is essential that the hydrolysis be as complete as possible; practically complete hydrolysis can be reached by prolonged boiling. The emulsion is then 'broken' by the addition of sulphuric acid of 60°Bé., and the contents of the vessels are allowed to settle, when separation into two layers takes place—an upper layer of fatty acids, and a lower aqueous one containing glycerin. The fatty acids are drawn off and washed, and are ready for subsequent treatment.

For the working up of the glycerin, *see Crude Glycerin from the Twitchell Process* under Oils, Fixed, and Fats.

6. **Saponification by means of ferment.** The explanation of the rationale of the Twitchell process attempted above, would seem to show that the action of the reagent is purely catalytic without any secondary reactions taking place, and resembles the action of ferments which accelerate hydrolysis without apparently undergoing any chemical change. The action of ferments as conditioning the initial stages of rancidity by effecting hydrolysis has been explained in the article Oils, Fixed, and Fats.

Connstein, Hoyer, and Wartenberg showed that the ferment contained in castor seed is capable of accelerating the hydrolysis of triglycerides to such a considerable extent that a technical process of saponification can be based on the action of the castor seed ferment.

The original *modus operandi,* in which ground castor seeds (together with their husks) were brought into an emulsion with oils (or fats) and water, slightly acidulated with acetic acid or acid salts, has been abandoned, as the formation of a most troublesome middle layer between the fatty and aqueous layers led to considerable losses of fatty matter and other concomitant drawbacks (low quality of glycerin, &c.). Even the use of decorticated seeds, although palliating the evil, did not remedy the inconveniences. The author's suggestion, viz. to isolate the ferment itself, has been worked out into a manufacturing process by Nicloux, who triturates decorticated castor seeds with castor or cotton seed oil, filters the mass through a fine silk gauze, and centrifuges the turbid oil so obtained. The residue remaining on the filter may be subjected again to the same process, but in practice it is thrown away as valueless. The turbid filtrate separates into three layers. The excess of oil forms the uppermost layer, the practically inactive aleurone grains and membranes fall to the bottom, whilst the cytoplasma, emulsified in oil, is found in the middle layer. This latter is used as the hydrolysing agent.

Hoyer also endeavoured to isolate the ferment, or at least to obtain preparations richer in active substance than the castor seeds themselves. Hoyer insisted on the necessity of working in an acid medium, but Nicloux found that the best technical results are obtained in a neutral medium (*e.g.* a solution of magnesium and calcium sulphates), and that it is advantageous, especially in the case of oils and fats containing glycerides of lower fatty acids, to remove the free acids by washing with soda. The retarding effect of lower fatty acids was confirmed by Hoyer, who found that the castor seeds contain an acid-forming water-soluble ferment, which produces sufficient acid to 'activate' the lipolytic ferment (Nicloux's 'lipaseïdin'), and which seems to consist of a mixture of volatile fatty acids and lactic acid. A series of experiments undertaken by Hoyer with a view to isolating the lipolytic enzyme by means of a mixture of light petroleum and chloroform led to the preparation of 'ferment-oil,' consisting of a mixture of castor oil and protaplasma (Nicloux's cytoplasma), and forming about 64 p.c. of the original castor seed.

This 'ferment-oil' has been replaced by the preparation 'ferment-milk' (termed in technical practice 'ferment'). The 'ferment' is obtained in the following manner: Decorticated castor seeds are ground up with a large quantity of water in a suitable mill, and the mass is filtered from the suspended solid substances, whereby a white creamy liquor is obtained. If this liquor is allowed to ferment spontaneously, water separates, and there rises to the top a thick creamy emulsion, consisting of 38 p.c. of castor oil fatty acids, 58 p.c. of water, and 4 p.c. of albuminoid substances. The latter constitute the actual lipolytic agent. Finally, it was found that a better 'activator' than magnesium or calcium sulphate is manganese sulphate, the addition of which to the emulsion has also been patented. (The accelerating action of certain metallic salts was first discovered by Pottevin.) In the manufacturing process oil or fat is introduced into a lead-lined vessel having a conical bottom, and provided with a steam-heating coil and a perforated coil for supplying compressed air. With the aid of the air current an emulsion is produced, whilst about 40 p.c. water, 5 to 8 p.c. of the 'ferment,' and 0·2 p.c. of manganese sulphate is introduced. After intermixture has been effected, the mass is allowed to stand for one or two or more days, according to the required amount of hydrolysis. During the first hours, the mixture must be observed carefully, as separation of the emulsified mass may occur. By stirring afresh, the emulsified state can be re-established, when the ferment begins to exert its action. When the desired degree of hydrolysis is reached the mass is warmed at 80°–85°, and 0·3 to 0·45 p.c. (reckoned on the fatty material) of a 50 p.c. sulphuric acid is introduced, whilst the mass is stirred (by air). The steam is then turned off, and the contents of the vessel are allowed to settle. The mass separates into three layers: (1) an aqueous layer at the bottom, containing glycerin; (2) a clear layer of fatty matter on the top; and (3) between these two a middle layer consisting of an emulsion of albuminoids, glycerin, fatty matter, and water. This middle layer is allowed to accumulate, and by warming and renewed treatment with water a further separation into three layers can be effected, so that the loss incurred by the formation of this middle layer may be reduced to the smallest possible amount. If the mass has been allowed to rest in the emulsified state for 24 hours, the fatty matter contains, as a rule, about 80 p.c. of free fatty acids. By allowing the ferment to act for 24 hours longer, a further 10 p.c. of neutral fat may be hydrolysed.

It is very important to ascertain for each individual oil or fat that temperature which is most suitable for it, and to maintain this whilst hydrolysis takes place. It is not advisable to allow the temperature to fall below 20°, and it is best to work at 2° or 3° above the melting-point of the fat. As the cytoplasma is readily destroyed when heated to 42° in contact with water, it is obvious that tallow is not a suitable material to be hydrolysed by this process, and it is difficult to obtain a product containing 75 p.c. of free fatty acids from a low-melting tallow, whilst high-melting tallows are not workable on a large scale. The hydrolysis of tallow can, however, be effected, if it be mixed with suitable oils or fats so as to reduce the melting-point of the mixture to below 35°.

The ferment must be used in as fresh a state as possible. The author observed that after a few days' standing the lipolytic power becomes greatly reduced. This would be readily explained by the fact, observed by Hoyer, that the 'ferment' is much more easily affected (injuriously) by acids than is the original castor seed pulp.

The glycerin obtained by this process has been described under *Fermentation Crude Glycerin* (*see* OILS, FIXED, AND FATS).

With the exception of the ammonia process

No. 4 and process No. 1, all the above described processes are employed on the largest scale in the candle and soap industries, as has been mentioned already incidentally. It need, therefore, only be briefly repeated that the processes enumerated under Nos. 2 and 5*b* and to a very small extent No. 5*c*, form the basis of the *stearine candle industry*, whereas the processes mentioned under Nos. 3 and 6 are practised in the *soap industry*. Process No. 5 is carried out on an immense scale, whereas No. 6 occupies only a very unimportant position in the soap industry. Recently also autoclave processes have been introduced into soap works (*see* SOAP).

Here we only deal with the working-up of the fatty matter, obtained after the removal of the glycerin in *candle works*.

AUTOCLAVE PROCESS.

According to the fatty material employed, the composition of the resulting fatty acids will naturally vary. The chief materials employed hitherto, at any rate in this country in the saponification processes (2), (5*b*) and (5*c*) described above, are tallow and palm oil, or a mixture of both; hence it may be taken that the fatty acids consist approximately of 50 p.c. of solid acids and 50 p.c. of oleic acid. Bone fat, especially on the Continent, is also largely 'autoclaved' for candle-making purposes. The kind of bone-fat employed for this purpose is the benzine-extracted, which is unsuitable for soap-making purposes. Since candles made exclusively from bone fat stearine are soft and friable, it is customary to make up the charges for the autoclave from a mixture of bone fat and other fats. With regard to goat's tallow as a candle material, *see* Lewkowitsch, ii. 642.

'Cotton seed stearine' of a high titer test—above 40°—is also used to some extent as a raw material for candle-making purposes.

In the United States such lard stearine as is unfit for edible purposes is not infrequently converted into candle material by the autoclave process. A sample of such material examined in the author's laboratory had the melting-point 51·7°.

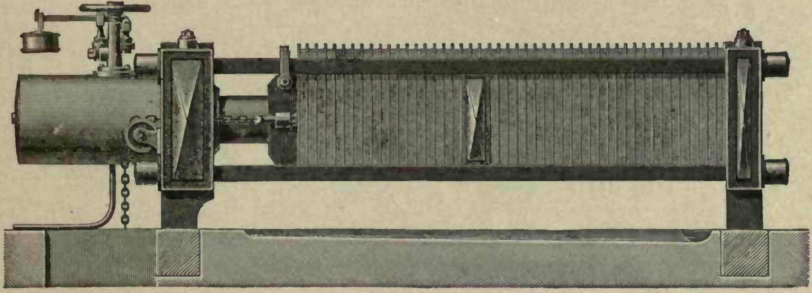


FIG. 7.

The employment of palm oil is somewhat restricted on the Continent, and other vegetable fats—such as vegetable tallow, shea butter, mowrah seed oil—are in use. The commercial exploitation of the large supplies of vegetable fats suitable for the candle industry has not yet, however, attracted such attention from importers as this subject deserves.

Since oleic acid is useless as a candle material, the next operation, after washing the crude fatty acids free from mineral acid, is to effect its removal from the mixed fatty acids. Hitherto this has been principally done by pressing the mixed fatty acids. The crude acids are run into shallow trays arranged in tiers, in which the fatty acids are allowed to crystallise. These trays are best placed in a room which can be kept at any desired low temperature; hence this room is fitted with cooling coils fed with cold brine from a refrigerating plant. The temperature at which the crystallisation takes place is carefully regulated, so as to obtain well-formed crystals of stearic and palmitic acids embedded in the mother liquor of oleic acid. If the fatty acids are cooled too rapidly, they solidify to an amorphous mass from which it is extremely difficult to express the oleic acid satisfactorily (*i.e.* the mass 'spues'). The solidified mass is taken out of the trays and pressed, at first at the ordinary temperature in a cold press, such as is shown in Fig. 7. The bulk of the oleic acid—'red oil'—is thereby removed. The hard cakes still contain too much oleic acid, and are therefore pressed a second time, at a somewhat higher temperature, in a hot press (Fig. 8), the cakes being placed in a bag of horse-hair or other suitable material, between press plates heated by live steam. In the figure shown, the steam is supplied from above; but since the stuffing-boxes, owing to the wear and tear to which they are subjected, require frequent renewing, the steam is supplied in more modern presses from below.

The cakes are allowed to stand under pressure when heated until a sufficient amount of oleic acid has been expressed to leave them white, ready to be melted (after a further purification to remove the last traces of lime) and to be moulded into candles. The oleic acid which runs from the hot-pressed cakes contains a considerable amount of solid acids ('stearine'). They are recovered either by adding the material to a fresh batch of the original fatty acids, or by subjecting it, together with the 'red oil,' to a process of cooling in a refrigerating house.

If the 'stearine' is not sufficiently white, the mixed fatty acids are subjected to distillation, previous to being pressed. For a method patented by Lanza for separating oleic acid from the solid acids by means of a dilute solution of stearo-sulphuric acid, *cp.* Lewkowitsch, Chem. Tech. iii. 175.

The 'stearine' contained in the 'red oil' (and in the runnings from the hot press) is recovered in the refrigerating house by cooling the liquid mass. Various appliances are in vogue. The simplest plan is to refrigerate the oil in large tanks fitted with a row of coils through which cooled brine or calcium chloride solution is pumped. Some manufacturers cool small quantities in mixing vessels, so as to be able to stir the cooled mass. The process requires attention, as the success of the operation depends on the separation of well-formed crystals. These are readily separated from the oleic acid by means of a filter-press.

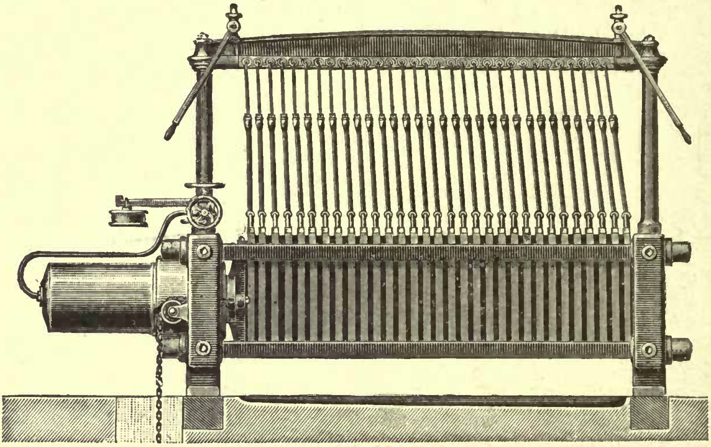


FIG. 8.

A more rapid method of cooling consists in allowing the red oil to run over a refrigerating wheel—Petit's wheel (Fig. 9). This wheel is shown partly in section. The cooled brine enters at C, runs along the circumference of the wheel, and leaves it at the opposite side. The oleine is fed into trough *f*, into which dips the rotating wheel, carrying with it upwards a thin film of oleic acid, which is thus rapidly cooled and deposits crystals of 'stearine.' The crystalline mass on reaching the scraper *h* is scraped off and the sludgy mass is collected in the cooled vessel F, from which it is pumped through pump P into a filter-press. The crystals form an intermediate product, and are mixed with the crude candle material at a suitable stage of the process.

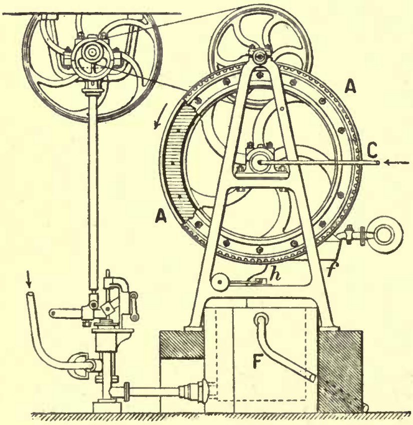


FIG. 9.

The yield of candle material by the *autoclave process* depends, of course, on the melting-points of the finished 'stearine,' and on the completeness with which the 'stearine' is recovered from the 'red oil.' It may, however, be taken as sufficiently accurate that the amount of high melting 'stearine' from tallow or palm oil, or a mixture of both, varies from 45–47 p.c. of the raw material, about 30 p.c. being obtained from the hot press and the remainder from the refrigerated 'red oil.' The proportion of finished oleic acid, 'oleine,' amounts to 47–48 p.c. In the case of good tallow, the yield of saponification crude glycerin of sp.gr. 1·240 reaches 10 p.c.

The 'stearine' is used as candle material either as such, or in admixture with paraffin wax, &c. (*see* CANDLES). The oleic acid, 'oleine,' is either converted into textile soap or used as a wool oil (*q.v.*). In the 'mixed process' (*see* below) part of the oleic acid is converted into 'candle material.'

If the fatty acids obtained by the autoclave process be too dark, and hence do not yield a sufficiently white candle material, they must be purified by distillation (*see* below). This is carried out in the apparatus described under *Acid saponification*.

During the distilling process the fatty acids do not undergo a chemical change, provided due care be observed in conducting the distillation. Since, however, the autoclaved mass contains some small proportions of unsaponified fat, which goes on accumulating in the still—especially if the still be fed continuously—decomposition of the unsaponified fat finally takes place with formation of hydrocarbons, which are produced somewhat rapidly when the accumulated neutral fat amounts to 12–15 p.c. of the still contents.

Acid Saponification Process.

The further working up of the sulphonated mass as obtained in process 5*b* is as follows :—

The sulphonated mass is run into boiling water and agitated by steam until the sulphonated compounds are hydrolysed. On standing, separation into two layers takes place : a lower aqueous layer containing the sulphuric acid employed and also the glycerol, and an upper layer of fatty material.

This fatty material is, as a rule, so dark that it cannot be worked up by pressing immediately after solidifying, in the manner described below. In order to obtain material of good colour the fatty mass must be distilled. A type of apparatus employed for this purpose is illustrated by Fig. 10. The fatty material, thoroughly freed from mineral acid by washing with water, is charged into still A, where it is heated at first by direct fire. When the material is sufficiently hot, a current of steam, dried preliminarily in P and superheated in S, is introduced through P_1, and the fatty acids are thus carried over through D, into the cooling worm R. The acids and the condensed water run into box X, where their separation takes place, and any vapours escape through G. The fatty material which is drawn off at Z, represents a mixture of liquid acids and candle material, which is pressed in the cold and subsequently when hot as described above. A large number of patents have been taken for special forms of stills and for processes claiming continuous feeding, distillation *in vacuô*, or both combined. The ovoid shape of the still shown in Fig. 10 has been largely replaced by stills of lenticular shape. In order to reduce the height to which the vapourised fatty acids must rise, the condensing arrangements also vary widely. In the plant shown in Fig. 10, the whole distillate is obtained in one mass. Some manufacturers collect the distillate in several fractions, whereby the subsequent separation into solid and liquid material is somewhat simplified. The portions distilling over towards the end of the ‘run are so dark-coloured and contaminated with organic impurities that they must be redistilled, hence they are termed ‘still-returns.’ For the exemplification of the distillation of such ‘still-returns,’ *see* Lewkowitsch, iii. 187.

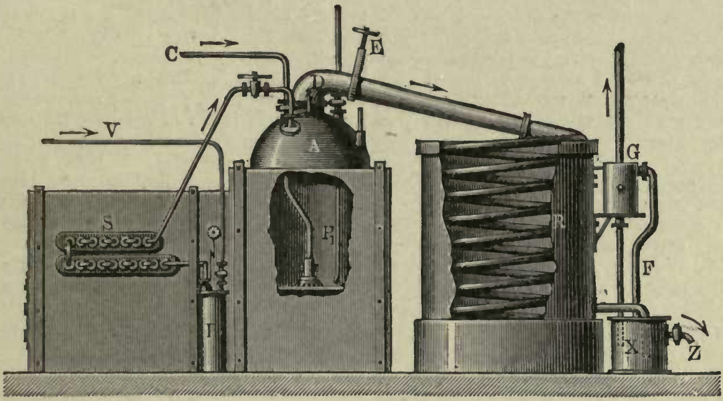


Fig. 10.

The best practice is to stop the distillation when dark-coloured distillates make their appearance and to remove the still residue into a second still, where the residues from several ‘runs’ are allowed to accumulate. These are then distilled separately, preferably *in vacuô*, and the distillation is carried so far that only pitch remains in the still.

The acid saponification process leads to a greater yield of solid material than does the autoclave process. Whereas the candle material obtained by the latter process can reach 52 p.c., the yield of ‘stearine’ by ‘sulphuric acid saponification’ is from 61 to 63 p.c. ; hence only 30–32 p.c. of oleic acid result as a by-product in this process, as against 47 p.c. from the autoclave process.

The conversion of oleic acid into candle material is of great technical importance and has formed one of the most important technical problems of the fat industry during the last 80 years. For a full description of the processes employed on a large scale the reader must be referred to Lewkowitsch, Chem. Tech. iii. 188.

The glycerin in the acid saponification process is obtained in smaller yield and, as has been shown under Glycerin, the quality is not as good as that obtained in the autoclave processes. Hence a combination of these two processes suggests itself, for as regards increase of candle material, the action of sulphuric acid on olein is apparently the same as on oleic acid. The combined method is known as the ‘mixed process.’

Mixed Process.

This process consists in hydrolysing the fatty material in an autoclave by means of bases, thus recovering the full amount of glycerin, and then treating the fatty material with concentrated sulphuric acid in the manner described above. Any neutral fat which has escaped hydrolysis in the autoclave is thus saponified. Therefore, in the subsequent distillation of the acidified material, less neutral fat can accumulate in the still than is the case when autoclaved, non-acidified, fatty acids are distilled. Hence the amount of hydrocarbons in the distillates is also reduced.

The yield obtainable from neutral fats by the 'mixed process is: candle material 61–63 p.c., oleic acid 32–30 p.c., crude glycerin, sp.gr. 1·240, 10 p.c., pitch and loss 2–3 p.c.

The product obtained by the Twitchell process, No. 5*b*, is too dark to be made into candle material by pressing, such as is feasible with autoclaved material. It is therefore imperative to distil the acids; it is advisable to treat the fatty material, previous to distillation, with concentrated sulphuric acid, as described above, so as to increase the yield of candle material.

The Twitchell process lends itself most advantageously to raw material of low quality and rich in fatty acids, such as 'greases,' which cannot be worked up economically by autoclaving. The yield from the Twitchell process is the same as that from the autoclave or from the mixed process, according to the manner in which the saponified material is treated, except in the case of cocoanut and palm kernel oils, where a notable amount of volatile acids is carried away with the steam during the prolonged time of steaming with the reagent.

"STEARINE"-CANDLE MATERIAL.

The solid material obtained by the above processes is known in commerce as 'stearine' and is chiefly employed in the manufacture of candles (*see* CANDLES). According to the process by which the stearine is obtained, we differentiate in commerce between 'saponification stearine' and 'distillation stearine.' The 'saponification stearine' originates from those autoclave processes which are not followed by distillation of the fatty acids. The 'distillation stearine' is obtained by all those processes in which distillation is employed in the last instance for the refining of the material.

The 'saponification stearine' consists practically of a mixture of stearic and palmitic acids.

The valuation of this material is based on its melting and solidifying points. The higher these are, the more valuable is the material. A definite iodine value indicates the amount of oleic acid left in the press cakes; a definite difference between the neutralisation and the saponification values corresponds to neutral fat that has escaped hydrolysis, and has not been pressed out with the oleic acid.

For commercial purposes it is but rarely required to ascertain the proportion of palmitic and stearic acids. If the direct determination of the stearic acid be too troublesome, the candle material may be valued on the basis of its solidifying points and of the neutralisation value.

'Distillation stearine' is also valued on the basis of its melting and solidifying points. These are usually lower than those of the 'saponification stearine.' The iodine value of a 'distillation stearine' furnishes a measure of the amount of 'iso-oleic acid' present; and the difference between the neutralisation and saponification values is a measure of the amount of lactone present. If the amount of hydroxystearic acid be required, the acetyl value must be determined. A complete analysis of 'distillation stearine' embraces the determination of the iodine value, of the neutralisation and saponification values, of the acetyl value, and the direct estimation of stearic acid; palmitic acid is then found by difference.

By means of the iodine value it is possible to differentiate 'saponification stearine' from 'distillation stearine.' The iodine value of the former rarely exceeds a few units, whereas 'distillation stearine' gives iodine values varying, as a rule, between 15 and 30.

The amount of unsaponifiable matter in both kinds of stearine should be negligible. The amount of the ash should be practically *nil*. It is important to determine the ash, as a definite amount, even 0·01 p.c. may lead to guttering of the candle prepared with such material.

J. L.

SAPONINS *v.* GLUCOSIDES and SENEGA.

SAPORUBRIN *v.* GLUCOSIDES.

SAPPHIRE *v.* ALUMINIUM; also CORUNDUM.

SARCINE *v.* HYPOXANTHINE.

SARCOLACTIC ACID *v.* LACTIC ACID.

SARD *v.* AGATE; ONYX.

SARDONYX *v.* AGATE.

SARSAPARILLA. (*Radix sarsæ*; *Racine de Salsepareille*, Fr.; *Sarsaparillwurzel*, Ger.) Of the various kinds of sarsaparilla imported into this country that variety which originally came by way of Jamaica, and is still known as 'Jamaica sarsaparilla,' is alone recognised by the British Pharmacopœia. It was formerly believed to be the root of *Smilax officinalis* (Kunth; Bentl. a. Trim. 289), but observations on a flowering specimen at Kew indicate that the official drug is derived from a distinct species to which Sir J. Hooker gave the name *S. ornata* (Lem.) (Pharm. J. [iii.] 19, 989). It is a woody climbing plant which inhabits Central America, especially on the mountains known as the Cordillera of Chiriqui in the isthmus of Panama adjoining Costa Rica, and perhaps other districts in the northern parts of South America. For botanical and other characters, *see* Pereira (Mat. Med. 3rd ed. 1153) and Flück. a. Hanb. 703. Sarsaparilla is an alterative medicine, employed especially in the treatment of some forms of syphilis, but it is not regarded with the same favour that it was formerly.

Of the constituents of sarsaparilla, with the exception of *starch*, which occurs to the greatest extent in some of the non-official varieties of the drug, the only ones to be described are a trace of *volatile oil* and the crystalline compound *parillin.* Little is known of the volatile oil. Pereira obtained only a few drops from the distillation of 140 lbs. of the root. This was heavier than water, was soluble in alcohol, and possessed the odour and acrid taste of sarsaparilla.

Parillin was discovered in sarsaparilla by Pallota in 1824 (Brugn. Giorn. 17, 386), who called it also 'pariglin.' Folchi soon afterwards obtained a similar substance, which he named 'smilacin'; similarly Thubeuf described 'salseparisin' (J. Pharm. Chim. 18, 734; 20, 162, 679), and Batka 'parillinic acid' (Annalen, 11, 313). Finally, Poggiale (J. Pharm. Chim. 20, 553) proved that these various products were one and the same compound, and for this he adopted the name 'smilacin.' 'Sarsaparillin' is another name for the same substance. See also Buchner (Rep. Pharm. 53, 1) and Petersen (Annalen, 15, 74; 17, 166). Flückiger, however, having reinvestigated the subject, adopts the term 'parillin,' as originally employed by Pallota (Arch. Pharm. [iii.] 7, 532; Pharm. J. [iii.] 8, 488). Parillin is deposited in a crystalline form, when an alcoholic extract of the root, after treatment with animal charcoal, is concentrated. When recrystallised from alcohol, it assumes the form of colourless needles. Flückiger precipitates the crude parillin from the concentrated alcoholic solution by the addition of water, and then purifies in the manner described. The yield was about 0·19 p.c. of the root employed. Air-dried parillin melts at 210°. Freed from water at 100°, it seems to have the formula $C_{40}H_{69}O_{18}$ or $C_{48}H_{85}O_{18}$. It is almost insoluble in cold, though somewhat soluble in hot water; is soluble in alcohol and less so in chloroform. Dilute (10 p.c.) sulphuric acid when heated with parillin gives a green colour, which on further concentration changes to red and brown. It is a glucoside, yielding by the action of dilute acids *sugar* and *parigenin*. The latter compound was obtained by Flückiger in scaly crystals from its solution in alcohol. It is distinguished from parillin by being quite insoluble even in hot water. Parillin and parigenin seem nearly related to saponin and sapogenin, if not also to cyclamin and cyclamiretin. A. S.

SARTON. A trade name of a preparation from the fruits or seeds of *Glycine Soja* (Sieb. and Zucc.), [*Soja hispida* (Mönch)], cultivated in China and Japan. Used in the treatment of diabetes.

SASSAFRAS OIL *v.* Oils, Essential.

SASSOLITE (*Sassolin* of D. L. G. Karsten, 1800). The mineralogical name for boric acid H_3BO_3. Although of abundant occurrence in solution in the Tuscan lagoons, it is not often met with in the solid state, but it was so observed by P. Mascagni around the 'soffioni' at Sasso in Tuscany. In the crater of Vulcano, one of the Lipari Islands, it occurs, however, in some abundance as a layer on native sulphur; and here it was formerly collected commercially.

L. J. S.

SATIN-SPAR and **SATINITE** *v.* Gypsum.

SATIN WHITE. A gelatinous aluminium hydroxide mixed with calcium sulphate and free lime, made by precipitating aluminium sulphate with excess of lime in fairly strong solution. Used in coating paper.

SAVIN, OIL OF, *v.* Oils, Essential.

SAXIFRAGIN *v.* *Barium nitrate*, art. Barium.

SAXON BLUE. A term occasionally applied to a solution of indigo in sulphuric acid. Used also as a synonym for smalt.

SAXON GREEN. *Emerald green* *v.* Pigments.

SCAMMONY *v.* Gum resins.

SCANDIUM. Sym. Sc. At.wt. 44·1. The discovery of *scandia* by Nilson in 1879 was an event of the greatest scientific interest, inasmuch as this oxide and its compounds have properties corresponding with those of the hypothetical element '*ekaboron*,' the existence of which had been predicted by Mendeleef to fill a gap in the periodic classification of the elements. The element, *scandium*, is distinguished from the allied metals of the cerium and yttrium groups by its low atomic weight and by the feeble basic strength of its oxide (Nilson, Ber. 1879, 551, 554; 1880, 1430, 1439; Compt. rend. 1879, 88, 645; 1880, 91, 56, 118; Cleve, *ibid.* 1879, 89, 419; Mendeleef, Ber. 1881, 14, 2821).

Occurrence.—In varying quantities in the following rare minerals: thortveitite (*q.v.*), ytterbite (gadolinite), euxenite, yttrotitanate, wiikite (Impilako, Finland, 1 p.c. Sc_2O_3), orthite (Impilako), auerlite, cerite, keilhauite, mosandrite, orangite, pyrochlore, äschynite, monazite, thorite, thorianite. Scandium is almost constantly associated with tin ores and is found in many specimens of wolframite (Crookes, Proc. Roy. Soc. 1908, 80, A. 516; R. J. Meyer, Sitzungsber. Akad. Wiss. Berlin, 1910, 398; 1911, 379; G. Eberhard, *ibid.* 1908, 851; 1910, 404; Zeitsch. anorg. Chem. 1908, 60, 134).

Separation and Purification.

1. *Fractional decomposition of the nitrates.* Aqueous solutions of the nitrates are evaporated until the normal nitrates crystallise; these salts are then decomposed by gradually raising the temperature when nitrous fumes are evolved and a vitreous mass of basic nitrates is produced. This product dissolves readily in hot water, and the cooled solution deposits the basic nitrates of the less electropositive rare earth metals. The operation is repeated systematically until scandium, neoytterbium, and lutecium are concentrated in the most readily decomposable fractions. Scandium nitrate is completely decomposed at temperatures at which neoytterbium and lutecium nitrates yield only basic nitrates (Nilson, *v. supra*; Marignac, Compt. rend. 1878, 87, 578).

2. *The basic salt method of separation.* The somewhat troublesome decomposition of the nitrates by heat is obviated by using Auer v. Welsbach's method of treating the oxides with insufficient nitric acid to convert all the bases into normal nitrates. The pasty mass is digested with alcohol when the normal nitrates dissolve leaving behind the basic nitrates. The decomposed fractions contain scandium, lutecium, and neoytterbium, the less decomposed fractions consist mainly of the basic salts of yttrium and the terbium group whilst the cerium metals remain as soluble normal nitrates and are thus completely eliminated. Erbium is separated from lutecium, neoytterbium, and scandium by adding water to the hot solution of the basic salts until a permanent turbidity is obtained, and digesting until the last-mentioned metals are precipitated, leaving erbium in solution (Monatsh. 1883, 4, 630; 1884, 5, 508; Schottländer, Ber. 1892, 25, 378).

Drossbach adapts the basic salt method to the chlorides instead of the nitrates (Ber. 1902, 35, 2826).

3. *Miscellaneous methods.* Scandium is separated from neoytterbium and lutecium by taking advantage of the circumstance that although in its slight electro-positive character the metal is allied to these elements of the yttrium group, yet it differs from them, and resembles the more electropositive cerium metals in forming a double potassium sulphate only very sparingly soluble in aqueous potassium sulphate (Nilson, *v. supra*).

Hydrochloric acid solutions of scandium when treated with solid sodium silicofluoride and boiled for 30 mins. give a precipitate containing this element free from the other rare earth metals. A separation from all these elements excepting thorium is effected by boiling a neutral solution with sodium thiosulphate when scandium thiosulphate is precipitated. Fractional sublimation of the anhydrous chlorides leads to a separation, scandium chloride being less volatile than the thorium salt. Boiling with excess of sodium carbonate brings thorium into solution, whilst the sparingly soluble scandium sodium carbonate $4Na_2CO_3,Sc_2(CO_3)_3,6H_2O$ is deposited (R. J. Meyer, Zeitsch. anorg. Chem. 1908, 60, 134; 1910, 67, 398).

Scandium hydroxide $Sc(OH)_3$ is precipitated by ammonia as a white gelatinous mass.

Scandium oxide (*scandia*) Sc_2O_3, white powder, sp.gr. 3·864, sparingly soluble in cold, easily soluble in hot, acids. The scandium salts with colourless acid radicles are themselves devoid of colour.

Scandium sulphate $Sc_2(SO_4)_3,6H_2O$ is extremely soluble in water; the double sulphate $Sc_2(SO_4)_3,3K_2SO_4$ is only slightly soluble in saturated solutions of alkali sulphates. **Scandium selenate** $Sc_2(SeO_4)_3,8H_2O$ forms rhombic prisms.

Scandium nitrate $Sc(NO_3)_3,4H_2O$ separates only from highly concentrated solutions, and when heated yields two basic nitrates.

Scandium chloride $ScCl_3$ and **bromide** $ScBr_3$ each crystallise with $6H_2O$; the **aurichloride** $3ScCl_3,2AuCl_3,21H_2O$ yellow needles, is very deliquescent.

Scandium platinocyanide

$$Sc_2[Pt(CN)_4]_3,21H_2O,$$

monoclinic prisms, crimson by transmitted, green by reflected, light, dissolving to a colourless solution.

Scandium borate $ScBO_3$, white powder, soluble in dilute acid, produced by fusing together scandia and boric acid.

Scandium salts of the fatty acids are more soluble in cold than in hot water; the **formate** $(HCO_2)_2Sc{\cdot}OH,H_2O$ and **acetate**

$$(CH_3{\cdot}CO_2)_2Sc{\cdot}OH,2H_2O$$

are crystalline; the salts of the homologous acids are amorphous (Crookes, Phil. Trans. 1908, 209, A, 15; 1910, 210, A, 359). These memoirs contain descriptions of many other scandium salts.

Scandium oxalate $Sc_2(C_2O_4)_3,5H_2O$, crystalline powder, soluble in ammonium oxalate and dissolving more readily in dilute sulphuric acid than the oxalates of other rare earth metals (Cleve, Compt. rend. 1879, 89, 419; Brauner, Chem. Soc. Trans. 1898, 73, 951).

Spectra.—Spark spectrum (Thalén, Compt. rend. 1880, 91, 45; Nilson, *v. supra*; Exner and Haschek, Ber. Wien. Akad. 1900, 109, IIa, 122).

Arc spectrum (Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904).

Arc spectrum in relation to solar spectrum (*v.* Lockyer and Baxandall, Proc. Roy. Soc. 1905, 538; Fowler, Phil. Trans. 1908, 209, A, 47).

G. T. M.

SCAPTIN *v.* DIGITALIS.

SCARLET, ATLAS, BIEBRICH, BRILLIANT, COCHINEAL, CROCEÏN, DOUBLE, *v.* AZO-COLOURING MATTERS.

SCARLET OCHRE. *Venetian red v.* PIGMENTS.

SCARLET RED (medicinal), *Fettponceau R.*

$$CH_3{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_3(CH_3){\cdot}N:N{\cdot}C_{10}H_6{\cdot}OH,$$

prepared from diazotised *o*-aminoazo toluene and β-naphthol, is a dark reddish-brown powder, m.p. about 185°. It is insoluble in water, sparingly so in cold alcohol, acetone, or benzene. One part dissolves in 15 of chloroform, and it is readily soluble in fats and fatty oils, and to a less extent in vaseline and paraffin. Pure scarlet red is used for stains in microscopical work, and has been shown to have valuable therapeutic properties (Fischer, Münchener Medizinische Wochenschrift, 1906, No. 42; Semaine médicale, 1908, 114).

It is applied in the form of an ointment to wounds, burns, ulcers, mallenders, bruised knees, &c., both in human and veterinary medicine, but it has only given successful results when applied to clean flat wounds of a fresh red colour. Being somewhat irritant, it should not be left in place continuously longer than a day. Its use depends on the power it possesses of forming thick resistant epithelial layers.

The ointment may be prepared by rubbing up 8 grms. of scarlet red with chloroform oil until the chloroform has evaporated, then adding enough yellow vaseline to form 100 grms. of ointment; according to Reinhardt the chloroform may be dispensed with. The ointment may also be prepared by rubbing together 1–2 grms. of scarlet red with equal parts of lanoline and *unguentum paraffine* to make 20 grms. The subcutaneous ingestion of scarlet red has also been investigated by Fischer; *see* also Werner, Münch. Medizin. Wochenschr. 1908, 2267.

Scarlet red gives a blue-green solution with sulphuric acid; on addition of water the colour becomes more blue than scarlet. Hydrochloric acid acts similarly, the colours being of a more reddish tinge, whilst nitric acid decomposes the stain. 0·5 grm. dissolved in 2–3 c.c. of boiling glacial acetic acid, and treated with a little zinc-dust, gives a transitory blue-red colour, which finally changes to a pale wine yellow. Drops of this liquid on filter paper become coloured dirty red-blue (Reinhardt, Aphotheker Zeit. 1909, No. 10). According to a note in the Pharm. J. 1912, 452, aminoazo toluene itself when used in the form of an 8 p.c. ointment is equally, if not more, effective than scarlet red. Both substances may be employed with advantage in blue ointment for syphilitic ulcers and as dusting powders in 4–8 p.c. strength with boric acid.

Literature.—Kracja, Münch. Medizin. Wochensch. 1908, 1969; Stoeber, *ibid.* 1910, No. 14; Kähler, Medizin. Klinik. 1908, 836; Wessley, *ibid.* 1910, No. 14; Bruhn, Therapeutische Neuheiten, 1908, No. 9; Gaudier, Rev. de Therapeutique, 1910, 671; Lemaire, Echo Medic. du Nord, 1910, June 12; Straus, Deutsche Medizin. Wochensch. 1910, No. 19; Pein, Therapie der Gegenwarf, 1910, No. 3; Köster, Zeitsch. Veterinärkande, 1910, No. 7; Picard, Rev. Gener. de medicine Vétérinaire, 1910, October 5.

SCARLET, WOOL, *v.* AZO- COLOURING MATTERS.

SCARLET, XYLIDINE, *v.* AZO- COLOURING MATTERS.

SCATOLEACETIC ACID, SCATOLECARBOXYLIC ACID *v.* INDOLES.

SCATOLES *v.* INDOLES.

SCHEELE'S GREEN *v.* ARSENIC.

SCHEELITE. Native calcium tungstate, $CaWO_4$, crystallised in the tetragonal system. For a pale-coloured, stony-looking mineral it is surprisingly heavy (sp.gr. 6·0), and it was consequently early known in Sweden as *tung-sten*, meaning 'heavy stone.' This name was transferred to the element discovered in this mineral by K. W. Scheele in 1781, whilst the mineral itself came to be known as scheelerz and later as scheelite. Well-shaped crystals are of frequent occurrence; these have the form of acute square pyramids, with distinct cleavages parallel to their faces. The colour is greyish, yellowish, or brown, and the lustre vitreous to resinous; hardness 4½. Analyses show the presence of up to 8 p.c. of molybdic acid replacing the tungstic acid; and the variety known as cuproscheelite forms a passage to cuprotungstite ($CuWO_4$). Scheelite is decomposed by hydrochloric acid with the separation of tungstic acid. Crystals of scheelite partly or completely altered to wolframite are found at Trumbull and Monroe in Connecticut, and at Kimpu-san in province Kai, Japan. These psuedomorphs from Japan have been incorrectly described as tetragonal iron tungstate under the name 'reinite.'

Scheelite occurs together with wolframite in veins of tin ore, and with gold in quartz-veins traversing granite and gneiss. As an ore of tungsten it is of much less importance than wolframite. By the ordinary methods of separation in water any scheelite present in the ore is collected with the wolframite, unless the latter is further separated from tin ore by the electro-magnet. At only a few places is scheelite mined alone, *e.g.* at Hillsgrove in New South Wales, the Otago gold-field in New Zealand, Parada in North Queensland, Hartley district in Rhodesia, California, and in Nova Scotia. Its uses are the same as those of wolframite (*q.v.*). L. J. S.

SCHLIPPE'S SALT. *Sodium sulphantimonate v.* ANTIMONY.

SCHORLOMITE *v.* TITANIUM.

SCHULTZE'S POWDER *v.* EXPLOSIVES.

SCHWARTZITE *v.* FAHL-ORE.

SCHWEINFURTH GREEN. *Emerald green v.* ARSENIC; also PIGMENTS.

SCHWEITZER'S REAGENT. A solution of hydrated cupric oxide in ammonia, used as a solvent for cellulose (*v.* CELLULOSE).

SCILLA, SCILLAIN, SCILLIN, SCILLIPICRIN, SCILLITIN, SCILLOTOXIN, *v.* SQUILL.

SCOPARIN, the colouring matter of the *Cytisus scoparius* (Link.), has been investigated by Stenhouse (Annalen, 78, 15), by Hlaziwetz (Annalen, 138, 190), and by Goldschmidt and Himmelmayer (Monatsh. 14, 202),

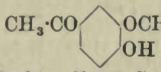
Scoparin $C_{20}H_{20}O_{10}+5H_2O$? crystallises in small yellow needles, m.p. 202°–219°, and is soluble in alkaline liquids with a pale-yellow colour. From a hot aqueous solution it is deposited on cooling in a gelatinous condition. The following derivatives have been prepared.

Hexacetyl scoparin $C_{20}H_{14}O_{10}(COCH_3)_6$, colourless prisms, m.p. 255°–256°; *hexabenzoylscoparin* $C_{20}H_{14}O_{10}(C_7H_5O)_6$, yellow crystalline powder, m.p. 148°–150°; *scoparin ethyl ether* $C_{20}H_{19}O_9(OC_2H_5)$, needles, m.p. 272°; and *acetyl scoparin ethyl ether*

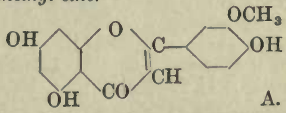
$$C_{20}H_{14}O_9(OC_2H_5)(C_2H_3O)_5,$$

needles, m.p. 140°–141° (G. and H.).

By fusion with potash scoparin gives *vanillic acid, protocatechuic acid, acetic acid,* and *phloroglucinol* (H.), and by the more gentle action of the alkali *phloroglucinol* and *acetylcatecholmonomethyl ether*



(G. and H.) (Perkin, Chem. Soc. Proc. 1899, 15, 123). With boiling hydriodic acid scoparin yields 1 molecule of methyl iodide and a new colouring matter *scoparein* (P.) is formed, which dyes shades almost identical with those given by luteolin. Scoparin itself is but a feeble dyestuff, and its tinctorial properties are almost indistinguishable from those of vitexin (*Vitex littoralis*) [A. Cunn.]. According to Perkin (Chem. Soc. Trans. 1900, 77, 423) scoparin is probably *methoxyvitexin*, and whereas vitexin is closely related to apigenin, vitexin is derived from *luteolin methyl ether*



A. G. P.

SCOPOLINE (*Oscine*) $C_8H_{13}O_2N$ is a vegetable alkaloid said to occur in crude belladonine (Merling, Ber. 1884, 17, 384). It is formed by boiling hydrochloric acid or baryta water with scopolamine or scopolamine hydrobromide (Ladenburg and Roth, *ibid.* 1884, 17, 151; Luboldt, Chem. Zentr. 1895, ii. 896; Arch. Pharm. 1898, 236, 11; Pinner, Chem. Zentr. 1898, i. 679; *see* also Hesse, Annalen, 1891, 261, 100; *ibid.* 1892, 271, 114).

Scopoline is a tertiary inactive base, containing one methyl group attached to nitrogen, and is closely allied to tropine, from which it differs by the substitution of one oxygen atom for two hydrogen atoms. It seems to contain no ketonic oxygen, but its consitution has not yet been fully determined (Schmidt, Chem. Zentr. 1905, i. 970; Arch. Pharm. 1909, 247; Ladenburg, Annalen, 1893, 276, 345; Hesse, *ibid.* 84; J. pr. Chem. 1902, [ii.] 66, 194).

It forms colourless, prismatic, very hygroscopic crystals, m.p. 109°, subliming at 90°, b.p. 241°–243°. Scopoline is readily reduced to *hydroscopoline* which contains two hydroxyl groups, and which, when oxidised with chromic acid, yields *methylpiperidine dicarboxylic acid* $C_8H_{13}O_4N,H_2O$, m.p. 214°–216°. Oxidised with chromic acid, scopoline yields pyridine methochloride, whilst when oxidised with barium permanganate it forms *scopoligenine* $C_7H_{11}NO_2$, m.p. 205°–206°, a secondary base which, when treated with methyl iodide is reconverted into scopoline. Scopoligenine forms a nitroso derivative $C_7H_{10}O_2N{\cdot}NO$, m.p. 174°–175° (Luboldt, *l.c.* 22; Schmidt, Arch. Pharm. 1894, 232, 409; 1905, 243, 559; Chem. Zentr. 1896, i. 1199).

Scopoline readily forms esters (Luboldt, *l.c.* 33).

Methylscopoline forms a light yellow thick fluid, b.p. 244° (decomp.), readily soluble in water, alcohol, or ether.

Acetyl scopoline $C_8H_{12}O_2N(COMe)$ is obtained by heating scopoline with acetic anhydride or chloride at 100°–130° (D. R. P. 79864). It has m.p. 53°, b.p. above 250°. Is readily soluble in organic solvents.

Benzoyl scopoline is obtained by the action of benzoic anhydride on scopoline, by the repeated evaporation of scopoline benzoate with dilute hydrochloric acid, or by the action of a current of the latter gas on an ethereal solution of scopoline and benzoic acid (D. R. P. 79864; Hesse, Annalen, 271, 119). It forms a crystalline mass, m.p. 68°–70°. *Cinnamoyl scopoline* is formed similarly. *Salicyl scopoline* forms needles insoluble in water, m.p. 105°.

A number of compounds of scopoline and its derivatives with the halogen and other acids, and also with platini- and auri-chlorides, are known (Schmidt, Chem. Zentr. 1902, ii. 844; D. R. P. 228204; and also nearly all the above references).

Tropyl derivatives of scopoline have been prepared by Luboldt (Arch. Pharm. 236, 40).

For the physiological action of scopoline and its derivatives, *see* Schiller (Chem. Zentr. 1896, ii. 1039).

The name scopoline was formerly given by Eykman to a glucoside which he isolated from the root of the *Scopolia japonica* (Maxim) (Rec. trav. chim. 3, 169; Pharm. J. 1884, 15, 81; Ber. 1892, 3078). This substance has the composition $C_{24}H_{30}O_{15},2H_2O$, forms needles, m.p. 218°, soluble in cold water and in alcohol, but not in chloroform or ether. Its solution in sulphuric acid has a blue fluorescence and decomposes on boiling thus:

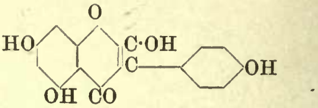
$$C_{24}H_{34}O_{15},2H_2O=C_{12}H_{10}O_5+2C_6H_{12}O_6.$$

SCUTELLARIN $C_{21}H_{20}O_{12},2\frac{1}{2}H_2O$ occurs in *Scutellariæ*, and in some other *Labeatæ* as *Galeopsis Tetrahit* (Linn.) and *Teucrium Chamædrys* (Linn.) chiefly in the leaves. It is readily prepared by treating an aqueous extract of the leaves and flowers of the *Scutellaria altissima* (Linn.) with 1 p.c. hydrochloric acid, and is thus obtained in the form of brownish-yellow needles. When pure it forms pale yellow needles, melting above 310°, sparingly soluble in alcohol, soluble in ammonia, alkalis, and alkali carbonates with a yellow colour. Alcoholic lead acetate gives a red precipitate, ferric chloride an intense green colouration passing to red on warming, and sulphuric acid a yellow solution. With strong acids in the presence of acetic acid orange crystalline salts are produced, which are unstable in the presence of water.

Acetylscutellarin, colourless crystals, melts at 267°. Fused with alkali, scutellarin gives *p*-hydroxybenzoic acid, and a very small quantity of a substance crystallising in large plates.

It seems probable that scutellarin is a glucoside, for though it is unaffected by dilute mineral acids, 30–40 p.c. sulphuric acid converts it into *scutellarein* $C_{15}H_{10}O_6$, readily soluble in alcohol. This yellow crystalline substance melts above 300°, gives with lead acetate an orange precipitate, and with ferric chloride a reddish-brown colouration. By fusion with alkali p-*hydroxybenzoic acid* and *phloroglucinol* are produced.

Scutellarein is isomeric with the kæmpferol described by Perkin and Wilkinson (Chem. Soc. Trans. 1902, 81, 585). It is probably an α-phenyl-γ-pyrone derivative, and may be provisionally represented by the formula—



(Molisch and Goldschmiedt, Monatsh. 1901, 22, 679). A. G. P.

SEALING-WAX. (*Cire à cacheter*, Fr.; *Siegellack*, Ger.) The Hindoos from time immemorial have possessed the resin lac, and were long accustomed to use it for sealing manuscripts before it was known in Europe. It was first imported from the East into Venice, and then into Spain; in which country sealing-wax became the object of a considerable commerce, under the name of Spanish wax. In mediæval times the composition contained bees-wax.

If shellac be compounded into sealing-wax immediately after it has been separated by fusion from the palest qualities of stick or seed lac, it then forms a better and less brittle article than when the shellac is fused a second time. Hence sealing-wax rightly prepared in the East Indies deserves a preference over that made in other countries, where the lac is not indigenous. Shellac can be restored in some degree, however, to a plastic and tenacious state by melting it with a very small portion of turpentine. The palest shellac is to be selected for bright-coloured sealing-wax, the dark kind being reserved for black.

The following proportions may be followed for making red sealing-wax. Take 7 oz. of shellac, 4 oz. of Venetian turpentine, and 3–4 oz. of vermilion. Melt the lac in a copper pan suspended over a clear fire, then pour the turpentine slowly into it, and soon afterwards add the vermilion, stirring the mixture briskly all the time with a rod in either hand. In forming the round sticks of sealing-wax, a certain portion of the mass should be weighed while it is ductile, divided into the desired number of pieces, and then rolled out upon a warm marble slab, by means of a smooth wooden block, like that used by apothecaries for rolling a mass of pills. The oval sticks of sealing-wax are cast in moulds, with the above compound in a state of fusion. The marks of the lines of junction of the mould-box may be afterwards removed by holding the sticks over a clear fire, or passing them over a blue gas-flame. Marbled sealing-wax is made by mixing two, three, or more coloured kinds of it while they are in a semi-fluid state. From the viscidity of the several masses, their incorporation is left incomplete, so as to produce the appearance of marbling. Gold sealing-wax is made simply by stirring gold-coloured mica spangles into the melted resins. Wax may be scented by introducing a little essential oil, essence of musk, or other perfume. If 1 part of balsam of Peru be melted along with 99 parts of the sealing-wax composition, an agreeable fragrance will be exhaled in the act of sealing with it. Either lampblack or ivory-black serves for the colouring matter of black wax. Sealing-wax is often adulterated with resin; in which case it runs into thin drops at the flame of a candle.

The following proportions are stated to form good sealing-wax :—

Red.—4 oz. turpentine, 5½ oz. shellac, 1½ oz. colophony, 1¼ oz. cinnabar, magnesia to colour.

Fine black.—4½ oz. Venetian turpentine, 9 oz. shellac, ½ oz. colophony, lampblack mixed with oil of turpentine as much as is required.

Black.—4 oz. Venetian turpentine, 8 oz. shellac, 3 oz. colophony, lampblack, and oil of turpentine.

Yellow.—2 oz. Venetian turpentine, 4 oz. shellac, 1¼ oz. colophony, ¾ oz. King's yellow.

Dark brown.—4 oz. Venetian turpentine, 7½ oz. shellac, 1½ oz. brown English earth (ochre).

Light brown.—4 oz. Venetian turpentine, 7½ oz. shellac, 1 oz. brown earth, ½ oz. cinnabar.

Dark blue.—3 oz. Venetian turpentine, 7 oz. fine shellac, 1 oz. colophony, 1 oz. mineral blue.

Green.—2 oz. Venetian turpentine, 4 oz. shellac, 1¼ oz. colophony, ½ oz. King's yellow, ¼ oz. mountain blue.

Gold.—4 oz. Venetian turpentine, 8 oz. shellac, 14 sheets of genuine leaf-gold, ½ oz. bronze, ½ oz. magnesia with oil of turpentine (Ure).

Sealing-wax that can be used without the need for a special flame in which to melt it is made by casting the sticks with a loosely woven wick running through the centre. When a light is applied to the wick it continues burning as long as required (Kressel, Eng. Pat. 13027, 1893 ; J. Soc. Chem. Ind. 1893, 1045).

For the preparation of the cheaper varieties of sealing-wax, used for sealing bottles, &c., the powdered ingredients may be simply mixed together and moulded into sticks under pressure, instead of being fused together (Watkins and Nunn, Eng. Pat. 15180, 1897 ; J. Soc. Chem. Ind. 1897, 815).

Sealing-wax that is insoluble in alcohol may be made : (1) By melting together 1 part of carnäuba wax and 1 part of hard paraffin, and adding, with constant stirring, 5 parts of red lead and 2 parts of whiting (J. Soc. Chem. Ind. 1900, 157). (2) By incorporating 3 parts of slaked lime with about 23 parts of molten colophony, thus forming calcium resinate to which is added a little heavy petroleum oil in order to render it less brittle (Ellram, Eng. Pat. 12176, 1899 ; J. Soc. Chem. Ind. 1900, 452).

Goldschmidt (Chem. Zeit. 1905, 29, 33) recommends the use of formaldehyde resins for preparing sealing-wax.

Elastic and flexible sealing-wax is made by mixing at 100°, 100 parts of gutta-percha or caoutchouc, 12·4 parts of lac, and 25 parts of rubber, dissolved in benzene (Schaar and Bergmeister, Fr. Pat. 391121, 1908 ; J. Soc. Chem. Ind. 1908, 1122).

SEAL OIL. Seal oil is obtained from the blubber of the various species of seal, such as *Phoca vitulina*, *Phoca grœnlandica*, *Phoca lagura*, *Phoca caspica*, &c.

The following seals are caught in the Antarctic Ocean : Weddell's seal (*Leptonychotes Weddelli*), sea-leopard (*Stenorhynchus leptonyx*), crab-eating seal (*Lobodon carcinophagus*), Ross's seal (*Ommatophoca Rossi*), sea-elephant (*Macrorinus leoninus*), Hooker's sea lion (*Arctocephalus Hookeri*).

In the early times of 'whaling,' the oil was exclusively 'tried' on board the whaling vessels, just as in the case of whale oil. Later, the seals were brought to rendering establishments on shore, and the blubber, cut from the animal, was thrown into large vessels of great height, in which the oil was pressed out from the lower layers by the superincumbent weight of the blubber, and the exuding oil was allowed to run off continuously. The oil running out at first was pale, and almost free from smell. When, however, the blubber became rancid and even putrid, the oil obtained was rich in free fatty acids, and besides acquired a dark colour and a nauseous taste and odour. At present, seal oil is recovered by more rational methods, such as will be described under the heading 'whale oil.'

According as the oil is extracted from fresh blubber on board the steamer, or from blubber which has been brought to shore, the colour of seal oil varies.

Crude seal oils deposit 'stearine' on standing, which is removed by filtering the oil. The 'stearine' is sold as 'fish stearine' or 'fish tallow' for soap-making and currying purposes. The 'stearine' from the first run oil is white and almost free from odour, whereas the 'stearine' obtained from the last rendered oil is dark, high in its proportion of free fatty acids, and of bad odour. This 'stearine' blackens easily on exposure to the atmosphere.

In commerce we find four qualities of seal oil, which are differentiated as 'water-white,' 'straw,' 'yellow,' and 'brown' seal oil ; these represent the oils as they are obtained successively from the blubber by 'rendering.' The darkest quality is that which has been the longest in contact with the animal tissue, and has been extracted at the highest temperature.

The oil from *Phoca fœtida*, occurring in the Baltic, differs notably from the seal oils furnished by the marine seals in respect of the iodine value. This must be attributed to the influence of food conditioned by the *fauna* of an inland sea. Such influence becomes more pronounced still in the case of the seal oil from *Phoca fœtida, var. saimensis Nordkvist*, a variety of seal which has adapted itself for many generations to the fresh water of the Saima lake. (For the characteristics of seal oil, *see* OILS, FIXED, AND FATS.)

Seal oil contains about 10 p.c. of palmitic acid and notable quantities of clupanodonic acid. The nature of the bulk of the seal oil fatty acids has not yet been investigated.

Seal oil is frequently adulterated with mineral oils and rosin oils, the detection of which is, however, easy. A mixture of seal oil with various fish oils is frequently sold as seal oil. The detection of the adulterant is not easy, as neither the iodine value nor the bromide test furnish decisive indications. In the present state of our knowledge the taste and smell alone render some assistance in the examination.

J. L.

SEBACIC ACID. *Ipomic acid.* (*Fettsaüre, Sebacinsaüre, Ipomsaüre*, Ger.)

$CO_2H[CH_2]_8CO_2H$.

Obtained by the dry distillation of oleic acid and of bodies containing oleic acid (Redtenbacher, Annalen, 35, 188) ; also formed when these bodies become rancid (Scala, Chem. Zentr. 1898, i.

439). Prepared by the action of caustic alkali on castor oil (Bouis, Annalen, 80, 303; 97, 34; Witt, Ber. 1874, 220); by the oxidation of spermaceti, stearic acid (Arppe, Zeitsch. Chem. 1865, 296), jalapin or jalapinic acid (Mayer, Annalen, 83, 143; 95, 160; Neison and Bayne, J. 1874, 625) with nitric acid; by the electrolysis of an aqueous solution of the potassium salt of the monoethyl ester of suberic acid and hydrolysing the diethyl ester thus formed (Brown and Walker, Annalen, 261, 121); by treating the condensation product of dibromobutane and magnesium with carbon dioxide (Gauthier, Ann. Chim. Phys. [viii.] 16, 350); also obtained from shellac (Endemann, Chem. Zentr. 1908, i. 1861). Has been synthesised from ethyl sodiomalonate and hexamethylene dibromide (Haworth and Perkin, Chem. Soc. Trans. 1894, 600). Sahlfield (Eng. Pat. 18940; J. Soc. Chem. Ind. 1896, 909) prepares sebacic acid by distilling wool grease or fulling grease from a retort, superheated to 300°, steam being injected into the neck of the retort. Sebacic acid crystallises in colourless nodular masses, m.p. 129° (Massol, Bull. Soc. chim. [iii.] 17, 746); readily soluble in alcohol or ether, sparingly soluble in water. On oxidation with nitric acid or permanganate, adipic, glutaric, and succinic acids are produced (Arppe, *l.c.*; Carette, Bull. Soc. chim. [ii.] 45, 270). By heating the acid with lime, sebacin $C_{10}H_{18}$, valeraldehyde and œnanthol are produced (Calvi, Annalen, 91, 110; Petersen, *ibid.* 103, 184). The anhydride melts at 78°–79° (Anderlini, Ber. 1894, Ref. 405). The esters of sebacic acid can be used in the manufacture of celluloid (Goldsmith and British Xylonite Co., D. R. P. 139738; Chem. Zentr. 1903, i. 749).

SECRETAGE. A process in which mercury or some of its salts is employed to impart to the fur of animals the property of felting.

SECURITE *v.* EXPLOSIVES.

SEED LAC *v.* RESINS.

SEIGNETTE'S SALT. (*Potassium sodium tartrate* $C_4H_4O_6KNa,4H_2O$ or *Rochelle salt.*) So named from having been discovered by Seignette, an apothecary in Rochelle, in 1672.

SELENITE. *Hydrated calcium sulphate* (*v.* CALCIUM; also GYPSUM).

SELENIUM. Sym. Se. At.wt. 79·2 (Pettersson and Ekman, Lenher, Meyer, *see* also Olivari, Atti. R. Accad. Lincei. 1908, [v.] 17, ii. 389; 1909, 18, i. 465; ii. 94, 264). This element was discovered by Berzelius in 1817 in the deposit of a sulphuric acid manufactured at Gripsholm, and is widely distributed in small quantities. It occurs native in cavities in Vesuvian lavas. In combination it is found as *sulphur selenide* or *selensulphur* in native sulphur; as *clausthalite* PbSe, *lehrbachite* PbSe,HgSe, *onofrite* HgSe,4HgS, *eucairite* $CuSe,Ag_2Se$, *crookesite* (CuTlAg)Se, and other minerals. It occurs in many varieties of copper and iron pyrites, especially in Norwegian pyrites, and is precipitated from the sulphuric acid prepared from them. It has been found by H. N. Warren in meteoric iron, and in the mineral waters from La Roche-Posay (Taboury, Bull. Soc. chim. 1909, [iv.] 5, 865).

Selenium is prepared from the deposit from sulphuric acid in the chambers and Glover's towers. The deposit is boiled with concentrated sulphuric acid and a quantity of sodium nitrate corresponding with the amount of selenium. The mixture is then diluted, stirred, and steam is blown through it till the sp.gr. is 1·25, the remaining oxides of nitrogen being expelled by a stream of air. The solution is filtered and the filtrate and washings are boiled with hydrochloric acid, after which the selenium is precipitated by a stream of purified sulphur dioxide. After washing and drying 99 p.c. selenium is obtained (Littmann, Zeitsch. angew. Chem. 1906, 19, 1081). Instead of sodium nitrate, potassium permanganate and sodium chloride may be used (Koch, D. R. P. 167457, 1903; J. Soc. Chem. Ind. 1906, 1220).

By a second method the chamber deposit is heated with concentrated potassium cyanide solution until it becomes grey. The solution, containing potassium selenocyanate, is filtered and treated with hydrochloric acid and sulphurous acid. The selenium is best purified by evaporation to dryness with nitric acid, subliming the selenious oxide so formed in a current of air and then dissolving it in water and precipitating selenium by means of hydrochloric acid and sulphur dioxide, the process being repeated several times (Threlfall, Proc. Roy. Soc. 1907, A, 79, 167).

Selenium, like sulphur with which it is isomorphous, exists in different allotropic forms (Coninck, Compt. rend. 1906, 142, 571; 143, 682; Coninck and Raynaud, Bull. Acad. Roy. Belg. 1907, 365; 1908, 57).

Amorphous selenium is formed as a finely divided brick-red powder when a solution of selenious acid is precipitated by sulphur dioxide gas, or when the acid is reduced by zinc, stannous chloride, or other reducing agents. It has a sp.gr. 4·26, and is soluble in carbon disulphide.

Semicolloidal red amorphous selenium is formed when solutions of dextrose and selenious or selenic acid are gently heated together. At 100° it is partially transformed into ordinary black selenium (Coninck and Chauvenet, Compt. rend. 1905, 141, 1234).

Colloidal selenium can also be obtained by dissolving in water the red selenium obtained by the reduction of selenium dioxide. The solution is blood-red, but assumes an orange-tint when sufficiently diluted with water.

Similar solutions are produced by the reduction of selenious acid in aqueous sodium protalbate or lysalbate with hydrazine hydrate or hydroxylamine hydrochloride. The precipitate is then dissolved in sodium carbonate and the solution dialysed. On gentle evaporation, stable red glistening flakes, completely soluble in water, are obtained (Paal and Koch, Ber. 1905, 38, 526). For other methods of producing colloidal selenium, *see* Ditmar, Chem. Zentr. 1905, ii. 741; Müller and Nowakowski, Ber. 1905, 38, 3779; Gutbier and Lohmann, Zeitsch. anorg. Chem. 1904, 42, 325; 1905, 43, 384; D. R. P. 164664, 1904.

Vitreous selenium is formed when the amorphous variety is heated to 217° and then rapidly cooled. It forms a brownish-black, brittle, glassy mass of sp.gr. 4·28, soluble in carbon disulphide. Like the ordinary amorphous selenium it does not conduct electricity. These three forms are generally regarded as all belonging to one allotropic modification and are sometimes known as 'liquid' selenium (Saunders, J. Phys. Chem. 1900, 4, 423).

The red crystalline form soluble in carbon disulphide, separates out when the latter is put into contact with amorphous selenium. This variety exists in two modifications, both belonging to the monoclinic system.

Metallic selenium is obtained when melted selenium is cooled quickly to 210° and then maintained at that temperature for some time (Littmann, *l.c.*; Marc, Ber. 1906, 39, 697), by placing amorphous selenium in contact with aniline or quinoline (Schrott, Chem. Zeit. 1906, 30, Rep. 384), or by fusing the vitreous form between carbon plates and then allowing to cool slowly (Coste, Compt. rend. 1905, 141, 715). When a solution in potassium hydroxide at 230° is allowed to cool slowly metallic selenium separates out in long needles, sp.gr. 4·82, and m.p. 219° (Coste, Compt. rend. 1909, 149, 674). Other varieties of metallic selenium melt at 210° and at 217°. Metallic selenium is more stable and less chemically active than the amorphous or red crystalline forms.

Grey crystalline metallic selenium also occurs in two modifications. One, A, forms round granular crystals stable at 140°, and in the dark, is a non-conductor of electricity; the other, B, formed when A is heated to 200° for some time or is exposed to light, forms longer crystals somewhat less soluble in carbon disulphide, and is a good conductor of electricity (Marc, Zeitsch. anorg. Chem. 1903, 37, 459; 1907, 53, 298; Ries, Physik. Zeitsch. 1908, 9, 228).

The electrical resistance of selenium is, in general, increased when heated and diminished considerably on exposure to light, the action being principally produced by the red rays (Marc, Zeitsch. anorg. Chem. 1906, 48, 393; 50, 446; and *l.c.*; Hesehus, Chem. Zentr. 1906, i. 1080). The change of conductivity is instantaneous, and is almost double in sunlight, but even the light from a small lamp has a noticeable effect. The resistance gradually returns after removal from light. On this property depends the construction of the *photophone*, in which light is converted into electricity (Carpini, Atti. R. Accad. Lincei. 1905, [v.] 14, 667).

For the use of selenium cells for spectrophotometric purposes generally, *see* Bloch, Compt. rend. 1901, 132, 914; Torda and Bornand, Eng. Pat. 4020, 1905; J. Soc. Chem. Ind. 1906, 91; Marc, *l.c.*; 1903, 37, 459.

A. Weinhold (Dingl. poly. J. 239, 160) has described the preparation of selenium resistance rods for photophonic purposes.

The electrical resistance of selenium is diminished by radium and Röntgen rays, and by the proximity of turpentine, of hydrogen peroxide (Bloch, *l.c.*; Aubel, Compt. rend. 1903, 136, 929), and of various pigments (Griffiths, *ibid.* 1903, 137, 647).

Selenium has also been used for observations of the transit of Venus and of the sun's eclipse.

Selenium has been employed in the production of coloured glass, a rose tint being obtained by the direct addition of selenium to the melting-pot. An orange-red colour is produced when cadmium sulphide is mixed with the selenium before adding the latter to the molten glass (Eng. & Mining J. Dec. 18, 1897, 731).

Selenium boils at 690° at 760 mm. (Berthelot, Compt. rend. 1902, 134, 75) forming a dark-red vapour of anomalous density at temperatures near the boiling-point but normal at 1420°, corresponding with the formula Se_2. In a high vacuum it boils at 310° (Krafft, Ber. 1903, 36, 1690, 4344).

Selenium is odourless and tasteless, but the vapour possesses an odour of putrid horseradish. It burns with a reddish-blue flame. In cold concentrated sulphuric acid it dissolves with a fine green colour, with formation of selenosulphur trioxide $SeSO_3$, from which solution selenium is precipitated by water. It mixes in all proportions with sulphur, crystals containing both elements in varying proportions being deposited from their solution in carbon disulphide (Rathke, Ber. 1903, 36, 594). Selenium can also replace sulphur in alums and in many organic compounds (Gutbier, Zeitsch. anorg. Chem. 1902, 32, 257; Frerichs, Arch. Pharm. 1903, 241, 177; Coos, Ber. 1902, 35, 4109; Chabrié and Bouchonnet, Compt. rend. 1903, 136, 376; Stollé and Gutmann, J. pr. Chem. 1904, ii. 69, 509; Becker and Meyer, Ber. 1904, 37, 2550; Edinger and Ritsema, J. pr. Chem. 1903, [ii.] 68, 72; Scott, Chem. Soc. Proc. 1904, 156; Smiles and Hilditch, *ibid.* 1907, 12; Michaelis, Annalen, 1905, 338, 267; 1907, 352, 152; Frerichs and Wildt, *ibid.* 1908, 360, 105; Simon, Monatsh. 1905, 26, 959; Taboury, Bull. Soc. chim. 1906, [iii.] 35, 668; Krafft, Ber. 1906, 39, 2197; Tschugaeff, *ibid.* 1909, 42, 49; Doughty, Amer. Chem. J. 1909, 41, 326).

Selenoantipyrine $C_{11}H_{12}N_2Se$ is prepared by treating antipyrine hydrochloride with potassium selenide or hydroselenide. It forms light yellow glistening crystals, m.p. 168° (Michäelis, Zeitsch. angew. Chem. 1901, 14, 1027; Annalen, 1902, 320, 1).

Selenium combines directly with many metals forming selenides; it reduces silver chloride in the cold, and gold compounds when heated to boiling, the metallic selenides being formed (Hall and Lenher, J. Amer. Chem. Soc. 1902, 24, 918).

Seleniuretted hydrogen SeH_2 is produced by the action of dilute hydrochloric acid on ferrous or alkaline selenide or by heating selenium in hydrogen gas, the quantity produced depending in the latter case upon the temperature. It decomposes when heated, so that when selenium is heated in hydrogen in a glass tube the hydride is at first produced, and is again reduced with deposition of crystalline selenium on the colder parts of the tube (Troutman, Bull. Soc. Ind. Mulhouse, 1891, 87; Pélabon, Compt, rend. 1894, 118, 142; 1894, 119, 73; 1895, 121, 401; 1897, 124, 360; Bodenstein, Zeitsch. physikal. Chem. 1899, 29, 429; Jones, Mem. Manch. Phil. Soc. 1904, 48, 1).

It is a colourless poisonous gas of persistent fœtid odour, more soluble in water than sulphuretted hydrogen, the solution being acid to litmus and absorbing oxygen from the air, with deposition of red selenium. It precipitates most heavy metals as selenides. The gas condenses to a liquid, b.p. −42°, which solidifies at −64°.

Selenium forms one oxide SeO_2, produced by evaporating selenium with nitric acid (Krafft and Steiner, Ber. 1901, 34, 560), or by heating the metal in dried oxygen, in white needle-shaped hygroscopic crystals, which sublime unmelted at about 300°, forming a yellow vapour (Coninck, Compt. rend. 1906, 142, 571).

Selenium dioxide yields yellow crystalline additive compounds with tetraethyl- and tetramethyl-ammonium chlorides, such as

$$SeO_2,2NMe_4Cl$$

(Carnevali, Atti. R. Accad. Lincei. 1908, [v.] 17, ii. 385).

Selenious acid H_2SeO_3 is produced by solution of selenium in nitric acid or of selenious oxide in hot water. It crystallises from solution in colourless prisms.

It is reduced by many organic substances, by sulphur dioxide in the presence of acid, or when exposed to the air, red selenium being formed (Coninck and Chauvenet, Bull. Acad. Roy. Belg. 1906, 81; Chabrié and Lapicque, Compt. rend. 1890, 110, 152).

A number of acid and neutral selenites are known. They are very poisonous and all evolve selenium when heated with ammonium chloride in a tube, or when acted on by certain moulds and bacteria (Gosio, Atti. Roy. Accad. Lincei. 1904, [v.] 13, i. 642), producing the horse-radish smell when heated on charcoal in the reducing flame owing to the formation of a carbon diselenide (Rathke, Ber. 1903, 36, 600).

Thiocyanoselenious acid $(HCNS)_2H_2SeO_3$ is described by Iwanoff (Chem. Zeit. 1908, 32, 468).

Selenic acid H_2SeO_4 may be produced by the action of chlorine or bromine on aqueous selenious acid. When selenites are similarly treated, selenates are produced.

Selenic acid is conveniently prepared by electrolysing a solution of selenious acid at 50°–60°, containing an excess of nitric acid and employing a current of 4–5 ampères per square cm. for about 100 c.c. of solution (Glausner, Chem. Zeit. 1907, 31, 630; Manuelli and Lazzarini, Gazz. chim. ital. 1909, 39, i. 50). Also by the electrolysis of lead selenate (Mathers, J. Amer. Chem. Soc. 1908, 30, 1374), or copper selenate (Metzner, Compt. rend. 1898, 127, 54). It cannot be obtained in the anhydrous condition by evaporation in air as it decomposes into oxygen, water, and selenious oxide at 280°. But if heated in a vacuum to 180° and then cooled, the product solidifies to a crystalline mass consisting of the pure acid (Cameron and Macallan, Chem. News, 1889, 59, 219). It melts at 58°; like sulphuric it chars organic matter, and combines eagerly with water forming a *monohydrate*, m.p. 26°, and also a *tetrahydrate*. Aqueous solution of this acid dissolves gold, copper, iron, and other metals, forming selenates, which closely resemble sulphates (Lenher, J. Amer. Chem. Soc. 1902, 24, 354); they are all reduced to selenites when heated with hydrochloric acid.

Selenic acid is reduced to selenium by formic, oxalic, malonic or pyruvic acid, and also by various aldehydes (Coninck and Chauvenet, *l.c.* 601).

Nitrogen tetroxide reacts with a concentrated solution of selenic acid cooled with solid carbon dioxide, forming the compound

$$SeO_2(ONO)_2$$

(Erdmann, Ber. 1906, 39, 1207).

Acids containing both sulphur and selenium are also known, as *selenosulphuric acid* H_2SeSO_3 and *selenotrithionic acid* $H_2SeS_2O_6$.

Selenium forms two *chlorides* and an *oxychloride* Se_2Cl_2, $SeCl_4$, $SeOCl_2$ (Lamb, Amer. Chem. J. 1903, 30, 209; Lenher and North, J. Amer. Chem. Soc. 1907, 29, 33), and the corresponding *bromides*, an *oxybromide*, and two *chlorobromides* $SeClBr_3$ and $SeBrCl_3$; but, according to Pellini and Pedrina (Atti. R. Accad. Lincei, 1908 [v.] ii. 78; 1909 [v.] 18, i. 463), selenium does not form compounds with iodine.

It forms complex compounds with the halogens and sulphur (Prandtl and Borinski, Zeitsch. anorg. Chem. 1909, 62, 237).

Selenium tetrafluoride SeF_4 is produced by the action of fluorine on selenium in a metal vessel. It is a colourless liquid boiling above 100° and solidifying at −80°. It is decomposed by water forming hydrofluoric and selenious acids and attacks glass rapidly (Lebeau, Compt. rend. 1907, 144, 1042). According to Prideaux (Chem. Soc. Trans. 1906, 320) a hexafluordide also exists (Lebeau, *l.c.*; and 1347; Ramsay, Compt. rend. 1907, 144, 1196).

Selenium nitride SeN is obtained by passing ammonia gas through a dilute solution of selenyl chloride $SeOCl_2$ in benzene. It is a brick-red, highly explosive powder (Lenher and Wolesensky, J. Amer. Chem. Soc. 1907, 29, 215).

Bartal (Chem. Zeit. 1906, 30, 810, 1044) has prepared a number of carbon compounds of selenium by the action of carbon tetrabromide on the latter, namely SeC_4; Se_2C_5; and also $Se_4C_9Br_2$; $Se_5C_{10}Br$; $Se_3C_3Br,3H_2O$; $Se_2C_3Br_2$ and $Se_4C_2Br_2$. The carbide CSe is also known.

Potassium selenocyanide is best prepared by mixing 70 grms. of pure potassium cyanide with 79 grms. of finely powdered commercial selenium, and fusing the whole at the lowest possible temperature. The mass is then digested on the water-bath for 3–4 hours with frequent additions of water, after which the resulting liquor is evaporated nearly to dryness and the residue dissolved in alcohol. Carbon dioxide is passed through the solution for about 2 hours, after which the liquid is filtered, the alcohol distilled off and the selenocyanide crystals are separated from their mother liquor by means of the filter pump (Schröder, Ber. 1900, 33, 1765).

Cyanogen triselenide is best prepared by spreading out potassium selenocyanide in a flat glass basin and mixing it with a third or half its weight of water, the pasty mass is stirred and a stream of nitrogen dioxide is passed through it, cyanogen and hydrogen cyanide being evolved during the whole process. The vessel should be surrounded by ice, and after the operation is about half completed small quantities of fuming nitric acid should be added from time to time. The product consists of a mixture of potassium nitrate and cyanogen selenide, the latter being removed by treatment with pure boiling benzene, which, on cooling, deposits the triselenide as yellow plates or prismatic needles, m.p. 132°. At 148·5° the triselenide decomposes with separation of selenium. It is decomposed by water and reacts vigorously with many organic substances, especially such as contain a labile hydrogen atom (Schröder, Ber. 1900, 33, 1765).

SEMICARBAZIDE, SEMIOXAMAZIDE, *v.* HYDRAZINES.

SENARMONTITE. *Antimony sesquioxide v.* ANTIMONY.

SENECA OIL. A name given to American petroleum, from the circumstance that it was collected by the Seneca Indians.

SENEGA ROOT. *Seneka, Snake Root. Senegæ Radix.* (*Racine de Polygala de Virginie*, Fr.; *Senegawurzel*, Ger.)

The root of *Polygala Senega* (Linn.; Bentl. a. Trim. 29), a plant inhabiting the central and northern portions of North America. It is a reputed diuretic and stimulating expectorant, especially applicable to chest diseases and rheumatism. Besides a trace of volatile oil and the constituents common to plants, senega root contains from 2 to 3·5 p.c. of *senegin* or *polygalic acid*, a compound which is nearly related to, if not identical with, saponin, as it occurs in soapwort and other plants. *See* Gehlen (Berzelius Jahrb. 1804, 112), Dulong (J. Pharm. Chim. 13, 567), Trommsdorff (N. J. Trommsdorff, 24, 2, 28), Quevenne (Berzelius Jahrb. 17, 309; 18, 394), Bolley (Annalen, 90, 211), Procter (Chem. News, 1861, 40), Christophsohn (J. 1875, 831), Kobert (Arch. Path. Pharmak. 23, 233, Hesse (Annalen, 261, 371). Senegin has the formula $C_{32}H_{52}O_{17}$ (Funaro, Gazz. chim. ital. 19, 21). To obtain it the root is exhausted with a mixture of two-thirds alcohol and one-third water, and the liquid, after concentration, is washed by shaking with ether. The syrup thus freed from fixed oil and other substances is precipitated by a mixture of ether (1 part) and alcohol (3 parts), and the crude senegin which falls is finally purified by solution in water, and reprecipitation by ether-alcohol (Procter). By the action of dilute acids it breaks up into *sugar* and *senegin*, thus:

$$C_{32}H_{52}O_{17}+2H_2O=C_{20}H_{32}O_7+2C_6H_{12}O_6$$

(Funaro) (*v.* GLUCOSIDES). According to Kobert, senega contains a second glucoside having acid properties, for which he adopts the name *polygalic acid.*

The 'virginic acid' of Quevenne and the 'isolusin' of Peschier have not been found by subsequent inquirers. A specimen of oil from the root of *Polygala Senega* had the sp.gr. 0·9616 at 18°; it appeared to contain olein, 73·9 p.c.; palmitin (with a little valerin), 7·9 p.c. (Schroeder, Arch. Pharm. 243, 628). Langbeck (Pharm. Zeit. 1881, 260) first detected methyl salicylate in old specimens of senega, which he supposed to be a product of decomposition of the root. Reuter (Arch. Pharm. [3] 27, 309) has, however, shown that the *volatile oil* of senega consists of a mixture of methyl salicylate and valerate.

For adulteration of commercial senega root, *see* Maisch (Pharm. J. [iii.] 20, 547; 21, 46). A. S.

SENEGAL GUM *v.* GUMS.

SENEGIN, SENEKA, SNAKE ROOT, *v.* SENEGA ROOT.

SENNA LEAVES. *Folia Sennæ.* (*Feuilles de Séné*, Fr.; *Sennesblätter*, Ger.)

This well-known purgative was introduced into European medicine by the Arabian physicians. As it now occurs in commerce, the drug consists of the leaves of *Cassia acutifolia* (Delile) and *Cassia angustifolia* (Vahl). The former species is found in Nubia and Kordofan, and produces what is known as Alexandrian senna. The latter is cultivated in southern India, and is the source of Indian or Tinnevelly senna (*cf.* Bentl. a. Trim. 90; Royle, Ill. Bot. Himal. 37).

Senna has frequently been the subject of chemical investigation. By different methods of treatment the earlier investigators have isolated various substances, but it is very doubtful if these represent definite constituents of senna (Braconnot, J. de Chim. Méd. 1, 284; Lagrange, Ann. Chim. Phys. 24, 3; Lassaigne and Fenuelle, *ibid.* [2] 16, 16; Bley and Diesel, Arch. Pharm. [2] 55, 257; Bourgoin, J. Pharm. Chim. [4] 5, 25; 12, 305; Ludwig, Arch. Pharm. [2] 119, 50; Dragendorf and Kubly, Pharm. Zeit. 1866, 4, 429, 465; T. B. Groves, Pharm. J. 1869, 10, 196; Stockmann, Pharm. J. [3] 15, 749; Stockmann and Seidel, Amer. J. Pharm. 1885, 557). The most important of these compounds is the cathartic acid discovered by Dragendorf and Kubly and independently by Groves. This is described as a colloidal glucoside which, in combination with calcium or magnesium, exists in senna, and to which the purgative action of the drug is due.

Tschirch and Hiepe (Arch. Pharm. 238, 427) obtained from an aqueous extract of senna leaves a yellowish crystalline deposit having the composition $C_{14}H_{10}O_5$. Also from the aqueous extract an impure cathartic acid was obtained by concentrating and adding alcohol, and this, when hydrolysed with dilute sulphuric acid, yielded yellow unstable *sennarhamnetin.* By percolating senna leaves with very dilute ammonia and precipitating the extract with hydrochloric acid crude *anthraglucosennin* was obtained, and when the ether extract of this was treated with toluene there remained yellow crystalline *glucosennin* $C_{22}H_{18}O_8$, a derivative of hydroxymethylanthraquinone, probably an emodin glucoside. From the toluene solution light petroleum precipitated orange-red crystalline *sennaemodin*, m.p. 223°–224°, which appears to be identical with aloe-emodin. The toluene solution also contained yellow crystalline *senna-chrysophanic acid* $C_{15}H_{10}O_4$, m.p. 172°, which was not precipitated by light petroleum. After the extraction with ether was complete, acetone extracted amorphous reddish-brown *senna-isoemodin* $C_{15}H_{10}O_5$, soluble in light petroleum, associated with sennarhamnetin, which is insoluble in this solvent. The residue consisted of black amorphous 'sennanigrin' (C 60·5, H 5·0 p.c., approx.) which yielded senna emodin and sennachrysophanic acid on hydrolysis with boiling alcoholic potash, and chrysammic acid when boiled with nitric acid.

The hydroxymethylanthraquinone derivatives, to which the purgative action of the drug appears to be due, were found to be present in a greater proportion in the fruits than in the leaves; but even in this case the proportion is much less than in *Rheum* or *Frangula.* The Alexandrian leaves were found to contain the largest, and the Tinnevelly leaves the smallest proportion of these compounds.

Senna pods appear to contain a greater proportion of cathartic acid than the leaves, and are said to be unattended by the nausea and the pain in the intestines which generally accompany the administration of the leaves (*see*

Macfarlane (Lancet, 1889, 164) and Salmon (Phar. J. [3] 20, 281). A. S.

SENNAAR GUM *v.* GUMS.

SEPIA. A dark-brown pigment prepared from a black juice secreted by certain glands of the cuttle-fish (*Sepia officinalis, Sepia Loligo,* &c.) and ejected by the animal to darken the water when it is pursued. One part of the juice is capable of making 1000 parts of water nearly opaque. The juice, when dried, yields a black mass, which, according to Prout, consists of 78 p.c. black pigment or melanin, 10·40 calcium carbonate, 7·00 magnesium carbonate, 2·16 alkaline sulphates and chlorides, and 0·84 mucus. The black pigment may be isolated by boiling the black mass successively with water, hydrochloric acid, and dilute solution of ammonium carbonate. It is a black, inodorous, and tasteless substance, quite insoluble in water, alcohol, and ether, but remaining suspended in water for a very long time; its deposition may, however, be accelerated by addition of acids or sal-ammoniac. It dissolves in warm caustic potash solution, forming a dark-brown solution, from which it is precipitated by sulphuric and hydrochloric acids, but not by nitric acid. It dissolves also in ammonia, but not in alkaline carbonates.

The pigment is prepared by saturating the dried native sepia with a little caustic lye, then adding more lye, boiling the liquid for half an hour, filtering, precipitating with an acid, washing the precipitate, and drying it at a gentle heat. It is of a dark-brown colour and fine grain.

Os sepiæ, Meerschaum, or *White fish-bone,* is the calcareous shell lying within the back of the cuttle-fish. It consists of two layers; the upper thin, but very compact, while the lower is thicker, but porous. The upper layer contains, according to John, 80 p.c. calcium carbonate with traces of phosphate, 9 gelatinous substance, insoluble in water and in cold lime-water, 4 water, and traces of magnesia. The lower layer contains 85 calcium carbonate with traces of potash, 4 gelatinous matter, and 4 water, with traces of magnesia. Forchhammer found in *Os sepiæ* 0·10 p.c. magnesium carbonate.

Os sepiæ is used as tooth-powder, for polishing, and for modelling for fine gold articles; it was formerly used as an internal remedy in cases of goitre.

SEPIOLITE *v.* MEERSCHAUM.

SEPTARIA (from *septum,* 'a division'), called anciently *ludus Helmontii* (the *quoits* of Van Helmont, from their form), are argillo-calcareous concretions intersected by veins of calcspar, which, when calcined and ground to powder, form an excellent hydraulic cement.

From the regular arrangement of cracks in septaria, which generally assume pentagonal forms resembling in appearance the divisions in the shell of a tortoise, they have received the common name of 'turtle stones' or 'fossil tortoises.' The turtle stones found in the Oxford clay at Weymouth, when cut into slabs and polished, form handsome tables. The number of veins of calcspar, upon which their beauty depends, renders these turtle stones unfit for forming an hydraulic cement, in consequence of their furnishing too great a quantity of lime when calcined. Septaria fit for furnishing cement are dredged in Chichester harbour and off the coast of Hampshire, and are also procured from Harwich, Sheppey, and several other places. A stratum of septarian stone, forming the Broad Bench on the coast of Dorsetshire, affords an excellent cement.

SEPTOFORM *v.* SYNTHETIC DRUGS.

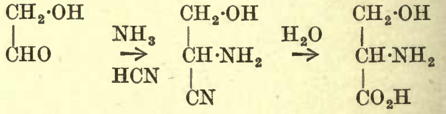
SERICITE *v.* MICA.

SERINE, *α-amino-β-hydroxypropionic acid*

$$HO{\cdot}CH_2{\cdot}CH(NH_2)CO_2H,$$

discovered by Cramer (J. pr. Chem. 1865, [i.] 96, 76) among the products of hydrolysis of silk-gelatin; has been similarly prepared from a large number of other proteids. Owing to the difficulty in separating serine the quantities obtained from most of these sources is less than 1 p.c.; silk-gelatin yields 6·6 p.c., and salmine 7·8 p.c. Serine occurs free in human perspiration, 1 litre affording 0·09–0·15 grm. of the β-naphthalenesulphonic derivative (Embden and Tachau, Biochem. Zeitsch. 1910, 28, 230).

Synthesis.—Fischer and Leuchs (Sitzungsber. K. Akad. Wiss. Berlin, 1902, 78) affected the first synthesis of serine by the action of ammonia and hydrogen cyanide on glycollic aldehyde, and subsequent hydrolysis of the amino nitrile thus produced—



$$\begin{array}{c} CH_2{\cdot}OH \\ | \\ CHO \end{array} \xrightarrow[HCN]{NH_3} \begin{array}{c} CH_2{\cdot}OH \\ | \\ CH{\cdot}NH_2 \\ | \\ CN \end{array} \xrightarrow{H_2O} \begin{array}{c} CH_2{\cdot}OH \\ | \\ CH{\cdot}NH_2 \\ | \\ CO_2H \end{array}$$

and they showed that on reduction with hydrogen iodide serine gives α-alanine, thus proving the compound to be α-amino-β-hydroxy-propionic acid.

A second synthesis is described by Erlenmeyer (Ber. 1902, 35, 3767), and Erlenmeyer and Stoop (Annalen, 1904, 337, 236), in which ethyl sodium hydroxymethylenehippurate

$$ONaCH : C(NHBz)CO_2Et,$$

obtained by condensing the ethyl esters of formic and hippuric acids in the presence of sodium ethoxide, is reduced by aluminium-amalgam to ethyl N-benzoylserine

$$OH{\cdot}CH_2{\cdot}CH(NHBz)CO_2Et,$$

which on hydrolysis yields benzoic acid and serine.

The most convenient method of preparing serine is a third synthetic process due to Leuchs and Geiger (Ber. 1906, 39, 2644), and really a modification of Fischer and Leuch's original method; ethoxyacetal $OEt{\cdot}CH_2{\cdot}CH(OEt)_2$, obtained by the action of sodium ethoxide on chloracetal, yields ethoxyacetaldehyde

$$OEt{\cdot}CH_2{\cdot}CHO$$

on hydrolysis, and this on consecutive treatment with ammonia, hydrogen cyanide and hydrochloric acid yields β-ethoxy-α-alanine

$$OEt{\cdot}CH_2{\cdot}CH(NH_2)CO_2H,$$

which on boiling with concentrated hydrobromic acid is converted into serine, the yield being 35–40 p.c. of the theoretical value calculated on the ethoxyacetal used.

***dl*-Serine.** Racemic or inactive serine prepared by any of the above synthetic processes, crystallises in thin colourless leaves, darkens at 225°, melts and decomposes at 246° (corr.); dissolves in 3–4 parts of hot water, or in 23·1 parts at 20°, and has a sweet taste (Fischer and Leuchs, *l.c.*).

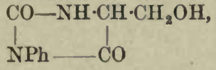
Derivatives.—The *methyl ester*

$CH_2(OH)\cdot CH(NH_2)CO_2Me$

is a strongly alkaline syrup forming a crystalline *hydrochloride*, m.p. 114° (corr.); the N-*benzoyl ethyl ester* $HO\cdot CH_2\cdot CH(NHBz)CO_2Et$ forms colourless crystals, m.p. 80°; N-*benzoyl*-dl-*serine* $HO\cdot CH_2\cdot CH(NHBz)CO_2H$ has m.p. 171° (Maquenne block); the *dibenzoyl derivative* $BzO\cdot CH_2\cdot CH(NHBz)CO_2H$ is sparingly soluble and melts at 124° (Maquenne block); p-*nitrobenzoyl*-dl-*serine*

$HO\cdot CH_2\cdot CH(NH\cdot CO\cdot C_6H_4\cdot NO_2)CO_2H$

forms bright yellow thin needles, decomposes at 206°–207° (corr.); *β-naphthalenesulphonic*-dl-*serine* $HO\cdot CH_2\cdot CH(NH\cdot SO_2\cdot C_{10}H_7)CO_2H$, has m.p. 214° (corr.); *phenylisocyanate*-dl-*serine* $HO\cdot CH_2\cdot CH(NH\cdot CO\cdot NHPh)CO_2H$ has m.p. 168°–169° (corr.), and yields the *anhydride*, *α-hydroxy-methyl-γ-phenylhydantoin*



m.p. 168°–169° (corr.).

l-**Serine.** The serine obtained from proteids is the lævo isomeride mixed with about 20 p.c. of the racemic compound (Fischer, Ber. 1907, 40, 1501); *l*-serine is obtained by the resolution of *dl*-serine through the fractional crystallisation of the quinine salts of the *p*-nitrobenzoyl derivative; it forms large prisms or six-sided plates, becomes brown at 211° (corr.), and decomposes at 228° (corr.), it is more readily soluble than the racemic compound, and has a sweet taste; it has $[\alpha]_D^{20}-6{\cdot}83^\circ$ in aqueous, or $+14{\cdot}45^\circ$ in normal hydrochloric acid solution (Fischer and Jacobs, Ber. 1906, 39, 2942).

Derivatives.—The *methyl ester*

$HO\cdot CH_2\cdot CH(NH_2)CO_2Me$

is a thick alkaline syrup, readily passes over into the *anhydride*, and forms a crystalline *hydrochloride* that decomposes at 167° (corr.); the p-*nitrobenzoyl derivative*

$HO\cdot CH_2\cdot CH(NH\cdot CO\cdot C_6H_4\cdot NO_2)CO_2H$

dissolves in 180 parts of water at 25°, and has $[\alpha]_D^{20}+43{\cdot}56^\circ$. l-*Serineanhydride* $C_6H_{10}O_4N_2$ decomposes at 247° (corr.) and has $[\alpha]_D^{20}-67{\cdot}46^\circ$ (Fischer and Jacobs, *l.c.*).

l-Serine is converted into *d*-alanine by the following series of reactions: methyl-*l*-*β*-chloro-*α*-aminopropionate, m.p. 157° (decomp.), obtained by the action of acetyl chloride and phosphorus pentachloride on the hydrochloride of *l*-serine methyl ester, yields on hydrolysis *l*-*β*-chloro-*α*-aminopropionic acid, which is reduced to *d*-alanine by sodium amalgam (Fischer and Raske, Ber. 1907, 40, 3717). The conversion of *l*-serine into *l*-cystine is effected by treating the hydrochloride of *l*-*β*-chloro-*α*-aminopropionic acid with barium hydrosulphide and oxidising the product with atmospheric oxygen in the presence of ammonia (Fischer and Raske, Ber. 1908, 41, 893).

d-**Serine** is obtained by resolution of *dl*-nitrobenzoylserine through the quinine salt and subsequent hydrolysis; it can be prepared also in good yield by allowing yeast to grow in a solution of racemic serine containing a large excess of sucrose, both isomerides are attacked by the yeast, but the lævo is destroyed far more rapidly than the dextro variety (Ehrlich, Zeit. Ver. deut. Zuckerind. 1906, 608, 840; Biochem. Zeitsch. 1908, 8, 464). In crystalline form, melting-point, and solubility *d*-serine is the same as *l*-serine, it has, however, a much sweeter taste, and has $[\alpha]_D^{20}+6{\cdot}87^\circ$ in aqueous, or $-14{\cdot}32^\circ$ in normal hydrochloric acid solution (Fischer and Jacobs, *l.c.*).

Derivatives.—The *copper salt* forms deep blue prisms insoluble in alcohol; the p-*nitrobenzoyl derivative* $HO\cdot CH_2\cdot CH(NH\cdot CO\cdot C_6H_4\cdot NO_2)CO_2H$ has m.p. 189·5° (corr.) with decomposition; is more readily soluble than the racemic compound, and has $[\alpha]_D^{20}-43{\cdot}74^\circ$ (Fischer and Jacobs, *l.c.*).

***iso*Serine**, *β-amino-α-hydroxypropionic acid* $H_2N\cdot CH_2\cdot CH(OH)CO_2H$ is not found naturally, nor does it occur among the products of hydrolysis of proteids. M. A. W.

SEROTIN *v.* GLUCOSIDES.

SERPENTINE. A rock much used as a decorative stone, and often popularly called a 'marble.' It has about the same hardness and density as ordinary marble, but is usually tougher and does not possess a crystalline texture. Essentially, it is a hydrous magnesium silicate, with more or less iron. An analysis by J. A. Phillips of serpentine-rock (sp.gr. 2·59) from the Lizard district, Cornwall, gave—silica, 38·86; alumina, 2·95; ferric oxide, 1·86; ferrous oxide, 5·04; nickel oxide, 0·28; chromic oxide, 0·08; magnesia, 34·61; potash, 0·33; soda, 0·77; water, 15·52 (Phil. Mag. 1871, [3] 51, 101).

Since this massive serpentine-rock consists mainly of a single mineral species, the name serpentine is also applied to the pure mineral. This is a hydrated magnesium silicate $H_4Mg_3Si_2O_9$, in which a small proportion of the magnesia is often replaced by an equivalent amount of ferrous oxide. It never occurs distinctly crystallised.

Serpentine, as a rock, usually exhibits dark shades of green and red, variously clouded and blotched, like the skin of a serpent, whence its name, as also the term *ophite* (ὄφις, a serpent), by which it is sometimes known. The rock may be veined with steatite, or rendered more or less porphyritic by enclosed crystals of bastite or bronzite, or may contain garnets, usually altered to kelyphite or chlorite, as may be well seen in the pyrope-bearing serpentine of Zöblitz, in Saxony. The beauty and variety of its colours have led to the extensive use of serpentine for vases and other ornamental objects. It is also employed for mantel-pieces and architectural columns, but the rock is usually so broken up by joints that it is difficult to procure slabs of large size. While valuable for indoor decoration, it is apt to yield on exposure to the atmosphere, gradually losing lustre and presenting an eroded surface. From its refractory behaviour on exposure to heat, it is sometimes employed in the construction of ovens. It has also been used as a source of certain magnesium salts, such as the sulphate.

Serpentine has been extensively worked in the Lizard district in Cornwall, but not elsewhere in Britain, though it occurs in Anglesea, in Ayrshire, and in Banffshire. The British serpentines have been specially studied by T. G. Bonney; an excellent account will be found in Teall's British Petrography, 1888, 104. On the Continent, serpentine has been worked for centuries at Zöblitz and elsewhere in Saxony. It is also wrought in the Vosges and in the departments of the Hautes Alpes, Lot, and Aveyron in France; while in Italy the most famous locality is at Prato in Tuscany, which yields a dark-green variety known as *verde di Prato*, resembling when polished an antique bronze, and hence largely used for statues, &c.

A fine translucent variety, known as *noble* or *precious serpentine*, of oil-green or yellowish-green tint, is worked at Snarum, in Norway. Pseudomorphs of serpentine after large crystals of olivine occur at this locality and retain in some cases a nucleus of the original mineral. It has been shown by Sandberger, Tschermak, Bonney, Roth, and others that most serpentines have been derived from peridotites, or rocks rich in olivine, though other minerals, such as hornblendes and pyroxenes, may also be converted into serpentine.

Several mineral varieties of serpentine have received distinctive names. *Picrolite* is the term applied to the mineral when presenting a columnar or fibrous structure, while an asbestiform variety with silky fibres is known as *chrysotile*. Much of the mineral used in the arts under the name of asbestos (*q.v.*) or amianthus occurs in veins running through massive serpentine, especially in Canada, and is really chrysotile. Serpentine with a lamellar structure is termed *marmolite*, and a shaly variety of dark-green colour from the Antigorio valley in Piedmont is known as *antigorite*. *Williamsite* is a translucent apple-green serpentine, found in limited quantity at a chromite mine at Texas in Pennsylvania, and cut as an ornamental stone. An exceptionally hard serpentine, termed *bowenite*, has been mistaken for jade, and C. A. McMahon has shown that the so-called jade of Afghanistan is of this character (Min. Mag. 1890, 9, 187).

Serpentine frequently carries chrome iron ore; and crystals of chromite and picotite are common microscopic enclosures in the rock. Native copper also occurs in serpentine, and large masses upwards of a ton in weight were obtained many years ago from fissures in serpentine at the Trenance mine, near Mullion, in Cornwall. Nickel ores and platinum also occur in association with serpentine-rocks.

It is not uncommon for serpentine to be intimately associated with limestone or dolomite, forming a rock known as *ophicalcite*, *ophiolite*, or *serpentinous marble*. The composite rock, being variegated with green and white colours, is prized as an ornamental material, but on exposure to atmospheric influences a differential action is set up, and the surface becomes unequally eroded. The famous *Verd antique* is a brecciated ophiolite (*v.* MARBLE).

For American serpentines *v.* G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903. L. J. S.

SERPENTINE-ASBESTOS *v.* ASBESTOS.

SERVICE BERRY. The seeds of the service berry (*Sorbus aucuparia*) contain about 22 p.c. of a yellow oil, sweet tasting, mobile, which rapidly dries on exposure to air, sp.gr. 0·9317 at 15°; refract. index at 15°, 1·4753; acid value 2·35; sapon. value, 208·0; iodine value, 128·5; iodine value of the fatty acids, 137·5; acid value of the fatty acids, 230·2 (van Itallie and Nieuwland, Arch. Pharm. 1906, 244, 164; J. Soc. Chem. Ind. 1906, 595).

SESAMÉ OIL (*Beniseed Oil, Gingelli Oil, Teel Oil*). Sesamé oil is obtained from the seeds of the sesamé plant, *Sesamum indicum* (Linn.), belonging to the family of *Bignoniaceæ*. The original home of *Sesamum indicum* is unknown. According to A. de Candolle, sesamé seed was brought from the Sunda Islands to India several thousand years ago, and has migrated thence through the Euphrates basin to Egypt.

India produces the largest amount of varieties; there the white seed, yielding the best Indian oil, is termed *suffettil*, whilst the black variety, containing the largest proportion of oil, is known as *tillie*. In the trade a mixture of white and dark seeds bears the name 'bigarré.'

According to the rules of the trade, white sesamé must contain at least 85 p.c. of white seeds. If the proportion of dark seed exceeds 15 p.c., an allowance is made. If the dark seed exceeds 25 p.c., the term white sesamé seeds no longer applies.

The bigarré quality must contain at least 35 p.c. of white seeds. The commercial seed known as 'grosses graines' must not contain more than 20 p.c. of 'petites graines.' No more than a maximum of 50 p.c. of small seeds is permitted; if they make up from 20 p.c. to 50 p.c., an allowance must be made.

By far the largest quantity of *Sesamum indicum* is grown in East India (the 1909–1910 crop amounted to 516,000 tons), Java, Siam, Tonkin, China, and Japan. Large quantities are also grown in the countries bordering the Mediterranean, especially in the Levant and Egypt. The seed grown in Africa belongs to the species *Sesamum radiatum*, Shum and Thonn.

Smaller quantities are produced in Algeria and on the West Coast of Africa, as also on the East Coast (Mozambique, Zanzibar, German East Africa). In Southern Rhodesia the seed is cultivated by the natives; it is not unlikely that in the near future it may be exported to Europe.

In South America, the plants are grown in Brazil and Venezuela, Mexico, the southern states of America, and in several islands in the West Indies. The chief emporium for the importation of sesamé seed into Europe is Marseilles, where all grades of sesamé oil from the Levant, the Indies, and West Africa are crushed.

Since the admixture of sesamé oil to margarine has become obligatory in Germany, Austria, and Belgium, a considerable sesamé oil industry has rapidly sprung up in these countries. The quantities consumed by these countries are in the inverse order, viz. Belgium, Austria, and Germany.

The sesamé oil industry has not been able to obtain a foothold in Great Britain, inasmuch as the finer qualities of sesamé oil, which are obtained in the first expression, do not find so remunerative an outlet as they do in other countries; in fact, the whole of the oil would have to be disposed of as soap oil. The small amount of seed imported into this country is used in the manufacture of compound cake (*see* Oils, Fixed, and Fats), the high proportion of oil in sesamé seed helping to bring up the percentage of oil in the mixed meal to the legally prescribed amount. The proportion of oil in sesamé seeds varies from 50 to 57 p.c.; hence the seed must be subjected to repeated expressions in order to yield the full amount of oil. The practical yields from sesamé seeds of different origin vary from 42 to 48 p.c.

The oils of the first expression in the cold represent the best qualities. The finest edible sesamé oil is obtained from the Levant seeds. Of these, the best brands are harvested in the Jaffa district. Slightly inferior in flavour to the Jaffa oil are the specimens obtained from seed grown in Caiffa, St. Jean d'Acre, Tarsus, Smyrna, Mersyna. The oil from Alexandretta seeds represents a lower grade still. The Indian seeds, embracing chiefly those from Kurrachee and Bombay, give oils of more unpleasant flavour, and are therefore not usable for the best kinds of margarine. Lower still, as regards taste and flavour, rank the oils from Chinese and African seeds. In China the seeds are roasted before being ground and expressed in wedge presses. Owing to this process the oil becomes dark-coloured and acquires a strong flavour of nuts. The largest quantities of Chinese sesamé oil are used in the German margarine industry.

The oils of second and third expression are used for manufacturing purposes, chiefly for soap-making. The average composition of sesamé cake is the following:—

	Per cent.
Oil	14·63
Moisture	7·65
Proteins	36·14
Ash	13·17
Crude fibre	4·83
Carbohydrates	23·58

When the seed does not arrive in a sound state, the oil is extracted with solvents for the complete recovery of the oil, and the extracted meal is sold as manure.

For the chemical and physical characteristics of sesamé oil, *see* Oils, Fixed, and Fats.

Sesamé oil contains from 12 to 14 p.c. of solid acids, the remainder consists of oleic and linoleic acids. Sesamé oil is dextro-rotatory, a property which may supply a useful additional means of identifying the oil. The optical activity is no doubt due to the presence of phytosterol and sesamin which form the bulk of the unsaponifiable matter in sesamé oil. In addition thereto, there occurs in the unsaponifiable matter a thick non-crystallisable oil which gives the characteristic colour reaction known as the 'Baudouin test' (*see* Oils, Fixed, and Fats).

The cold-drawn sesamé oil is largely used as an edible oil, notably so, as pointed out above, in the manufacture of margarine. Since small quantities of sesamé oil are easily revealed by the Baudouin test, it has been made obligatory in Germany and Austria to use at least ten parts of sesamé oil in the manufacture of margarine for 100 parts of fatty matters. In Belgium, 5 p.c. are prescribed. The best oils are consumed as table oils; small quantities of this class are used in the production of perfumes ('enfleurage').

The best cold-drawn oil being rather high in price, adulteration of the best qualities with poppy seed oil, cotton seed oil, and arachis oil is not infrequent. The sesamé oils of second and third expression are adulterated with rape oil.

The lower qualities of sesamé oil find a large outlet for soap-making in the south of Europe; they are also used as burning oil and for making india-rubber substitutes. J. L.

SEWAGE. The problem of sewage purification has been gradually forced on the country owing to the evils arising from the pollution of the streams, and to the increased flow of sewage resulting from the general introduction into our towns of the water-closet system, viz. water-borne sewage. Another source of pollution, although less serious than that of sewage, is manufacturing refuse.

Sewage may be defined as the water supply of a town after it has been used. It contains the solid and liquid excreta of the population, household drainage, containing a great variety of animal and vegetable remains derived from the food, the bathing, and the washing of the household.

With the exception of a few towns sewered on a dual system of drainage, sewage also contains the washings of the street, and storm water, and in any large community trade waste of a complex character forms a part of it.

The separate system of drainage is only sanctioned by the Local Government Board in cases where surface water can be discharged by separate drains without creating a nuisance, and where combined system would be unduly costly.

Water-borne sewage never has the same composition in any two cities, and in any given sewer the character of the sewage varies with the hour of the day, the season of the year and the state of the weather.

The creation of Rivers Boards in 1891, and subsequently of River Authorities to enforce the provisions of the Rivers Pollution Prevention Act, 1876, directed inquiry into the practical efficiency of the systems of sewage disposal in operation in works of sanitary authorities, and revealed the great difficulties experienced by these bodies in devising means and maintaining works for the efficient purification of the sewage of their districts. Especially has this been so in the case of the County and non-County Boroughs in England, and it has been found necessary to insist on more efficient means being adopted for the effectual purification of the sewage by these authorities.

The first and necessary step to take in the purification of sewage is to remove as much of the matters in suspension as is economically possible. On arriving at the outfall works the sewage is usually passed through coarse screens of various design. In large works, automatic appliances are provided. Then the sewage is passed through detritus tanks designed so that the speed of flow will allow the heavier and mineral matters to settle out of the sewage, leaving the lighter mineral and organic suspended matters to pass forward with the sewage to tanks for further treatment. Tank treatment may have for its object:—

(*a*) The removal of the remaining suspended matters in the sewage by quiescent sedimentation or continuous flow sedimentation (sedimentation tanks).

(*b*) Sedimentation with partial digestion of the insoluble and soluble organic matters (septic tanks); or

(*c*) Sedimentation aided by the use of various chemicals causing a flocculent precipitation and more rapid settlement of suspended matters (precipitation tanks).

The choice of tank treatment depends upon a number of factors affecting the particular sewage under treatment. The quality of the sewage, the time required to effect a maximum reduction of the suspended solids, and the economical concentration of the sludge produced have to be considered having regard to the final treatment of the sewage by filtration. Some sewages contain more solids which settle very slowly than other kinds, and no precise rules can be laid down as to the design of the tanks or as to the period of settlement required; but with regard to the holding capacity of the tanks, the minimum requirements for sedimentation, septic, and chemical precipitation tanks are fixed by the Local Government Board Regulations (*see* p. 666).

The 'septic tank treatment' of sewage has not fulfilled the claims that were put forward on its introduction as to the advantages of the treatment. It was primarily claimed that it solved the sludge difficulty, inasmuch as practically all the organic solid matter was digested in the tank. Experience has shown, however, that only a small percentage of the organic solids are digested, the amount varying to some extent with the character of the sewage, the size of the tanks relative to the volume treated, and the frequency of cleansing. It was also said that sewage which had passed through a septic tank was more easily oxidised than sewage from which the solids had been allowed to settle, either with or without the aid of chemicals, in tanks which were frequently cleaned out; but here again experience has shown that septic tank effluent is not more easily oxidised than the other liquids. The septic tank does not effectively remove the suspended solids in the sewage, the tank liquid containing on an average from 10 to 15 grs. of suspended solids per gallon—an amount that materially affects the maintenance of the filters used for the final purification. Moreover, a slow rate of flow through the tanks tends to increase the risk of nuisance from smell, when the septic effluent is distributed over a filtering area. The sewage ought not to remain more than 24 or less than 12 hours in a septic tank. The longer the tank is run without cleaning the less *volume* of sludge there will be per given volume of sewage treated, but the amount of suspended solids issuing from the tank increases seriously as time goes on and greatly affects the efficient working of the filters and the quality of the filtrate. On the other hand, the main use of a septic tank, owing to its large capacity, is, that it has the effect of equalising the sewage as regards strength, and of keeping the character of the liquid uniform, and the Royal Commission (5th Report) think that in certain circumstances the adoption of septic tank treatment as a preliminary process is efficient and economical.

If there be any advantage in attempting to ferment the organic solids of sewage, it would appear preferable to avoid the disturbance of the sludge in the bottom of the tank through the evolution of gas by separation of the sludge from the flowing sewage and to submit the sludge to septic treatment in a special chamber provided for the purpose. This principle has been carried out to some extent by Travis, who has devised a hydrolytic tank and installed the process at Hampton. The tank is so designed that only a small proportion of the sewage comes in contact with the sludge, but difficulties in preventing nuisance and the efficient removal of the suspended matter have prevented its general adoption. In the septic tank designed by Imhoff, and known as the Essen tank, the flowing liquid is entirely separated from the sludge. The tank is of cylindrical form with a conical bottom. In the upper portion of the tank is a sedimentation chamber with sloping floors and slots at the bottom to allow the sludge to settle into the sludge chamber below (Surveyor and Municipal and County Engineer, 1909, 625). It is claimed that the sludge which is withdrawn from this chamber from time to time contains only 75 p.c. water and is non-putrefactive, and that a large percentage of the organic solid matter is destroyed. The method has been adopted by the Emscher Genossenschaft, but there has been so far no experience with it in English sewage works.

With regard to the chemical precipitation of sewage, it has long been known that no amount of chemicals which can with any show of reason be added to sewage is sufficient, or nearly sufficient, to convert the whole of the putrescible matter into harmless forms. All methods of chemical treatment of sewage, by patented processes or otherwise, aim at clarification and purification; that is, the separation of the solids and the clarification of the liquid, usually by chemical precipitants. Mere precipitation processes cannot, however, be relied upon to remove sufficient of the soluble putrescible organic matter to prevent the effluent subsequently becoming offensive to the senses. The treatment of the sewage by chemical precipitation, whilst effecting considerable purification, at the same time brings the effluent into a condition more suitable for subsequent filtration, especially where the deposition tanks are small for the volume of sewage to be treated. Hence the use of chemicals can only be recommended for the purpose of starting a process of purification, and the only practicable way of purifying the soluble putrescible organic matters of the liquid sewage resulting from the precipitation process is to resort to filtration. That filtration in some form or another is essential to any efficient system of sewage purification has been established over and over again, and insisted upon by high authority. It is therefore important that we should understand the scientific principles involved in the process of filtration which are available for the purpose. We must first define what is, or ought to be, the true aim of sewage purification. It is to remove the suspended matters, and to convert the carbon and the nitrogen of the remaining organic matter in the sewage into inorganic matter. The River Pollution Commissioners in 1868, with this aim in view, advocated filtration through land. They laid down conditions essential for successful results which are as true to-day as they were at that date, although subsequent researches have thrown new light on the true causes of the conversion of the organic matter into inorganic matter and assisted materially to a more satisfactory solution of the problem. They found that in filtration, whether through sand, gravel, chalk or soil, or through a mixture of chalk and sand, it was essential that the atmospheric oxygen should have frequent and free access to the interior of the filter, and that the effluent should flow freely off from the bottom of the filter, so that as the last portion of each dose of sewage water sinks into the filter it may draw atmospheric air into the pores of the material from the surface downwards. They regarded the action as a mechanical and chemical one, and showed that the action could be maintained if the oxidising powers of the filtering material were not allowed to become choked. The subsequent researches of Schloesing and Muntz in France (Compt. rend. 1884, 301; 80, 1250) and of Robert Warington in England (Chem. Soc. Trans. 1877) have shown that purification as defined above is brought about by the intervention of living organisms. Sewage contains various kinds of organic matter which furnish abundant food for bacteria, which are always present in great numbers.

The changes brought about in the condition of sewage on standing may be of a twofold character. The one, due to living organisms requiring free oxygen for their growth, has the result of rendering the organic matter inoffensive. The other, due to organisms which flourish in the absence of free oxygen, gives rise to products which are offensive. The oxygen necessary for the growth of what may be termed the aerobic organisms is usually derived from the oxygen dissolved in the water which carries the sewage; but sewage itself is either entirely free from, or at any rate contains less dissolved oxygen than is necessary for the active growth of these aerobic organisms. In consequence of the absence of dissolved oxygen in sewage, it has during its passage to the outfall works already begun to undergo change of a putrescent character owing to the growth of the putrefactive or anaerobic organisms. The products of this putrefactive change rapidly absorb free oxygen passing into more stable forms, and therefore when sewage is poured into a river or into fresh water it rapidly robs the water of its dissolved oxygen, and if the quantity poured in exceeds a certain proportion as compared with the river or fresh water, the whole of the water is deprived of its dissolved oxygen and becomes incapable of supporting the activity of the aerobic organisms, whilst at the same time the activity of the putrefactive or anaerobic organisms may render the whole of the waters noxious.

The kind of decomposition which sewage undergoes is therefore determined by the kind of microbes which can freely develop and remain active in sewage, and the kind of microbes which can develop and remain active is, in turn, determined by the access or exclusion of air and light, by temperature, and by the chemical reaction of the whole. These facts are of prime importance, for they furnish the basis of all good systems of sewage disposal. The prompt disposal of sewage is the end and aim of any rational system of sewage disposal. Putrefactive processes are slow and often a menace to the health of a neighbourhood.

Processes of oxidation are more rapid and complete and are inoffensive. Warington showed that, under favourable conditions, these living organisms in sewage may be so cultivated as to effect the destruction of the organic matter, provided the filter is well supplied with air requisite for the discharge of the functions of these organisms, and also that sufficient mineral matter of a suitable kind be present to combine with the products of their action. The results of the experiments made by the American chemists (1891) of the Massachusetts Board of Health, confirm this statement, for they say:—

'The purification of sewage by intermittent filtration depends upon oxygen and time; all other conditions are secondary. Temperature has only a minor influence; the organisms necessary for purification are sure to establish themselves in a filter before it has long been in use. Imperfect purification for any considerable period can invariably be traced either to a lack of oxygen in the pores of the filter or to the sewage passing so quickly through that there is not sufficient time for the oxidation processes to take place. Any treatment which keeps all particles of sewage distributed over the surface of sand particles, in contact with an excess of air for a sufficient time, is sure to give a well-oxidised effluent, and the power of any material to purify sewage depends almost entirely upon its ability to hold the sewage in contact with air. It must hold both sewage and air in sufficient amounts. Both of these qualities depend upon the physical characteristics of the material. The ability of a sand to purify sewage, and also the treatment required for the best results, bear a very close relation to its mechanical composition.'

Plants built to answer the above conditions consist of a number of sand beds, each of about one acre superficial area and from 4 to 5 ft. in depth, carefully levelled, underdrained and divided from each other. Crude sewage, after passing through a grit chamber and screens to remove road washings and large floating substances, is run successively upon the various beds, none of the beds receiving sewage for a longer period than 6 hours out of each 24, for if the beds received the sewage continuously there would be absolutely no air present at any time in the bed, and air is necessary for the life of the aerobic organisms. By applying the sewage only 6 hours out of the 24, as the liquid drains out of the bed, air enters to take its place, and the conditions favourable to the action of both groups of organisms are maintained. By this process from 50,000 to 75,000 gallons of domestic sewage, sewage not containing a large proportion of manufacturing waste, can be purified each day on one acre of sand-bed area, so that the polluting substances are to such an extent removed that the liquid, as it runs away from the bed, is clear, bright, almost odourless, and can be emptied into a very small stream without fear of causing trouble (L. P. Kinnicutt).

The application of sewage to land is carried out by two processes, which are known as intermittent downward filtration and broad irrigation. In the former, the land is used after the manner of an ordinary sand filter and requires the land to be open and porous with a sandy subsoil. With land of a retentive character, with a clay subsoil, broad irrigation is usually adopted, the sewage being distributed over the land in such a manner that it runs over the surface, and the purification is effected by the nitrifying organisms in the surface soil. As some irrigation areas are, however, underdrained in order to assist the land to 'dry off' sufficiently rapidly, a certain amount of downward filtration may take place, and it is therefore difficult to make a distinction between the two processes in every case. In both intermittent downward filtration and broad irrigation it is desirable to intercept some of the suspended solids in the sewage before applying the liquid to the land. In sewage farming proper, the preliminary treatment is very slight and usually consists of straining and rough settlement.

The volume of sewage that can effectively be purified on a given area of land varies within wide limits, depending on the quality of the land and the strength of the sewage. The general experience is that on good land a sewage of average strength, from which the major portion of the suspended solids have been eliminated by tank treatment, can be treated at about the rate of 30,000 gallons per acre per day, with the production of a high-class effluent. With unsuitable land, such as clay, not more than 3000 gallons per acre can be efficiently treated, even after settlement of the sewage.

The Local Government Board require, when the sewage after previous sedimentation is applied to land of the most suitable kind by broad irrigation, that the quantity should not exceed 4500 gallons of dry weather flow per acre per day, or the dry weather flow sewage from 150 persons. Surplus land must also be provided in such cases from 25 p.c. to 50 p.c. for resting purposes. When the land is less suitable the quantity per acre may be reduced to as little as 1000 gallons per day. When the sewage, after previous sedimentation, is applied to downward filtration on land, the quantity per acre of the most suitable land shall not exceed 15,000 gallons of dry weather flow per acre per day, or the sewage from 500 persons. Surplus land up to 25 p.c. is usually required. This area to be increased if the land be not of the best. When the sewage, after chemical precipitation, is applied to land, the tank effluent may be applied at the rate of 30,000 gallons per acre per day, or the sewage from 1000 persons as a maximum.

Land naturally varies in its physical character and in its power to purify sewage. Moreover, climatic conditions play an important part, and although the volume of sewage which land is capable of dealing with is sufficient to warrant the smaller sanitary authorities in adopting land filtration, and it is the cheapest of all systems in such cases, yet it has been successfully contended that in many cases, especially in the great centres of manufacturing industry, the land available is either of unsuitable quality, is available in quite inadequate area for effective filtration through the soil, or is obtainable only at a prohibitive cost, and it is now recognised that sewage purification may, in such cases, be carried out on comparatively small areas artificially prepared.

Artificial sewage filters may be divided into two broad classes: contact beds and percolating filters.

Contact-bed treatment. This method is the result of experiments made by W. J. Dibden, on London sewage. It differs from intermittent downward filtration in that the sewage instead of being applied slowly and allowed to drain through the land, is run rapidly into a watertight bed, filled with a coarse material as cinders, clinkers, or coke, and retained in the bed for a given number of hours, after which the liquid is quickly run out of the bed. The bed, after it is emptied, is allowed to remain empty for some time before receiving the next filling. The beds are usually built on two levels so that if sufficient purification is not accomplished by single contact, the liquid from that bed can be run upon a second bed at a lower level and receive double contact.

The method is not adapted for treating crude sewage or sewages containing much suspended matter, and the capacity of a contact bed is best maintained by preventing, as far as possible, the access of suspended and colloidal matters to the bed.

The physical, chemical, and bacterial changes which take place during the process of purification in a contact bed are complicated. The formation of colloidal film deposits on the surface of the filtering medium, and the action of micro-organisms are essential to the process. In order to regulate the growth of this slimy deposit so that the bed will do its proper work, and at the same time not lose its liquid capacity, it is essential to carefully regulate the cycle of operations, especially providing a period of rest for the bed to remain empty before refilling, as the resting period is the most important phase of the cycle, when oxidation is most active. A bed should not be filled more than three times in 24 hours, and the fillings should be as far apart from one another as practicable, viz. three fillings in three cycles of 8 hours each, so that the maximum period for drainage and aeration between the fillings may be obtained.

The depth of contact beds should not exceed 6 ft. or be less than 2 ft. 6 ins. In deciding upon the size of the material to be used, the amount of suspended matter in the liquid to be treated must be considered. As a general rule, the greater the amount of suspended matter in the liquid the larger the material should be. Material of a diameter from $\frac{3}{8}$ to $\frac{5}{8}$ of an inch down to as fine as $\frac{1}{4}$ inch diameter may be used. Over the drains of the beds, material of fairly large size must be laid, and in order to preserve the life of a contact bed, it is advisable to retain as much as possible of the suspended matter upon the surface of the material by using fine material for the top six inches or so.

In practice it has been found necessary in some instances to wash the filtering material when it has become clogged, and in a few of the larger installations this operation is carried on continuously. Not only has this to be done on account of accumulated solid matters derived from the sewage passed to the bed, but is in part due to the consolidation and disintegration of the material of which the bed is formed. Whether it is more economical frequently to wash or renew the material in contact beds, or to remove the greater portion of the suspended matters from the sewage liquid before it is treated and to wash the beds less frequently, depends primarily on local circumstances, yet it is important to state that the troubles arising from clogging are generally traceable to (*a*) the employment of inferior material forming the bed, (*b*) allowing too much suspended matter to be carried forward with the tank effluent, (*c*) overworking the filters. There is therefore a limit to the economical use of 'washery' plant in connection with the working of contact beds.

Percolating filters. In percolating filters the sewage is not held up, but is allowed to percolate through the filter in the presence of air and the organisms on the surface of the filtering medium. Clinker and coke are preferable materials to form the filtering medium, presenting the roughest and most irregular surfaces.

The grading of the material is largely influenced by the presence or absence of suspended matters, and by the amount of 'removable' organic matter in the sewage effluent applied to the filter. In practice, material of ¼ inch diameter (fine material) is the smallest grade used for liquids containing little or no suspended matter, but the usual grade employed is not less than 1½ ins. to 2 ins. diameter.

The most usual form of filter is circular in plan, this form being adopted because the distribution of the sewage is most frequently effected by means of revolving sprinklers which cover a circular area. The floor of the bed should be constructed of concrete of sufficient thickness to form an impervious stratum over which the drainings from the bed can flow. Upon this floor, a false tapered tiled floor is constructed, leaving air and drainage spaces between the tiles, aeration of the bottom part of the bed with effective drainage being essential in order to obtain a fully oxidised effluent and to enable the bed to excrete the solid matter which passes from it.

The external walls are usually constructed by honeycombed brickwork providing ventilation of the sides of the filters. The depth of the filter is controlled, on the one hand, by the strength of the sewage to be treated, and on the other hand, by the size of the filtering material, and it is generally assumed that a filter is capable of purifying a quantity of sewage proportionate to its depth.

Efficient and equable distribution of the effluent over the surface of the filter is essential, and there are many devices used for this purpose, the class of automatic revolving distributors being mostly employed. The Candy-Whittaker distributor is capable of automatically dealing with any flow between 150 and 1600 gallons per square yard of bed per 24 hours without the employment of an automatic valve or dosing chamber. The effluent from percolating beds contains suspended matters which it is essential to remove. Secondary sedimentation with or without shallow cinder filtration forms, therefore, an integral part of most percolating filter plants.

Percolating filters are better adapted to variations of flow than contact beds, and are less liable to become clogged.

The Royal Commission found that where the sewage effluent contains much suspended matter, it is usually advisable to construct percolating filters of coarse material, *whatever the strength of the original sewage.* Moreover, in nearly every case a greater rate of filtration can be adopted if the material is arranged in the form of a percolating filter than if it is used in contact beds. The rate of filtration per cube yard in the case of percolating filters may, generally, be double or nearly double that which is permissible in the case of contact beds.

'During the past ten years, data have been collected at the Lawrence Experimental Station (Massachusetts State Board of Health) as to the part played by carbon compounds (other than carbonates) in sewage and sewage purification. Determinations of the carbon content and loss on ignition of evaporation residues, showed that in the case of residues from sewage, carbon formed, on the average, 23 p.c. of the total residue and 50 p.c. of the loss on ignition, the corresponding figures for residues from other products being: surface waters, 7·5 and 26; sewage effluents from filters of coarse material, 10 and 36; wool scourings, 17 and 54; and paper mill waste, 23 and 61 respectively. The ratio of carbon to organic nitrogen in the different products was as follows: sewage, more than 11½; surface waters, 16–20 sewage effluents, 6½–7½; wool scourings, 21; paper mill waste, 14½. In a number of sewage sludges, nearly one-half of the organic matter consisted of fatty substances, and the carbon content of the sludge was about 55 p.c. of the loss on ignition. In sediments from trickling or contact filters, the carbon content was 50 p.c. of the loss on ignition. Septic tank sludge contains 56–61 p.c. of carbon, and the carbon content of the fatty substances therein is about 25 p.c. of the total carbon. In the case of sands from sewage filters, a considerable portion of the loss on ignition may be due to chemically combined water. In some specimens examined, the carbon content was 7–12 times as high as the organic nitrogen, and on the average was about 35 p.c. of the loss on ignition. Experiments were made to determine the maximum oxygen consumed by boiling with permanganate till no further reduction of the latter took place (8 hours usually sufficed), and the results were compared with the oxygen consumed in two minutes, and with the amount of oxygen theoretically necessary to oxidise the carbon content of the sewage, &c. In unfiltered sewage, the two minutes "oxygen consumed" was 10–19 p.c. and the maximum "oxygen consumed" 34–54 p.c. of the theoretical value, whilst in filtered sewage, the corresponding figures were 13–28 and 51–86 p.c. respectively, and in effluents and waters the percentages were still higher. The clogging of sewage filters is due chiefly to non-nitrogenous carbon compounds (cellulose, fats, &c.). In the matter retained by the filters, the amount of carbon is about seven times as high as that of organic nitrogen. About 75 p.c. of the carbonaceous matter stored in the filter is contained in the first foot in depth. A study of nitrification in sewage has indicated that if the carbon content of the sewage is 10 times that of the nitrogen, nitrification will not take place. If the nitrogen content be increased, nitrification begins, but may again be checked by increasing the carbon content' (H. W. Clark and G. O. Adams, J. Ind. Eng. Chem. 1911, 3, 738–742).

Based upon the recommendations contained in the Fifth Report of the Royal Commission (1908), the Local Government Board adopted their revised and supplementary requirements (1909) with respect to sewage purification schemes (Sanitary Engineering, Moore and Silcock, vol. 2, appendix iii.).

Quantity of sewage to be treated. The quantity of sewage per head of population is usually reckoned at the rate of 30 gallons per day for dry weather flow for domestic purposes. If there be trade refuse to be dealt with this must be added.

The quantity of sewage and rain-water to be *fully* treated at the works is: 3 times the domestic sewage plus $1\frac{1}{10}$ trade refuse, and the quantity of sewage and rainfall to be *partially* treated in storm beds is 3 times the domestic sewage plus $1\frac{1}{10}$ trade refuse. Any excess over these quantities may be discharged over the storm-water overflows.

Storm overflows. Storm overflows on sewers should as far as is reasonably practicable be avoided, but when they are necessary they should be placed in such positions and with the weirs so fixed that no nuisance is likely to result. In any district where there is an active river authority, the Board will desire to be informed of the opinion of such authority in respect of any proposed overflows. In the absence of any special circumstances, overflow weirs should be fixed so as not to come into operation until the flow exceeds six times that of the average dry-weather flow.

There should be no overflow for untreated sewage or storm-water at or near the disposal works.

Screens. All liquid delivered at the disposal works should, as a rule, be passed through a screening chamber.

Storm-water treatment. A weir set at three times the dry-weather flow should be placed *below the screens,* and any volume passing over this weir should be dealt with in storm tanks. The tanks should be two or more in number and their total capacity should not be less than a quarter of the dry weather flow. They should be so arranged that when they are full they will act as 'continuous flow' tanks, and that they can be readily emptied and kept empty when no liquid is passing into them.

The liquor from the tanks can be discharged without further treatment except in special cases, and the sludge should be dealt with by any of the usual methods which may be most suitable in the particular circumstances.

In cases where a sufficient area of suitable land is available for the purpose, detritus tanks followed by irrigation may be substituted for the storm tanks.

SEWAGE TREATMENT.

Detritus tanks. There should be two or more detritus tanks below the screening chamber. The capacity of each tank should be about $\frac{1}{100}$ of the dry-weather flow.

Septic tanks. Septic tanks should not be less than two in number, and their total capacity should be about equal to the dry-weather flow.

Chemical precipitation tanks. For *quiescent* treatment there should not be less than eight tanks, each of which should have a capacity equal to about two hours' dry-weather flow.

For *continuous flow* treatment there should not be less than two tanks, with a total capacity of at least eight hours' dry-weather flow, and in most cases a greater number of tanks will be desirable.

Settling tanks. For *quiescent* treatment, same as chemical precipitation tanks.

For *continuous flow* treatment there should not be less than two tanks, with a total capacity of from 10 to 15 hours' dry-weather flow.

Filters. In determining the sizes of percolating filters and contact beds, the Board have, in order to allow for the strength of the sewage to be treated, adopted the divisions into 'strong,' 'average,' and 'weak' sewages recommended by the Royal Commission.

The strength of sewage should, when possible, be ascertained by analysing average samples of crude sewage taken in dry weather at frequent and regular intervals throughout seven days, and in proportion to the flow. Possibly, in the case of small works, the period for taking samples for analysis might be somewhat shorter, but the period should not be less than 48 hours, and Saturday and Sunday should be avoided.

In every case, the daily rainfall during the period when the samples were being taken and during the seven preceding days should be ascertained.

The analysis should, in all cases, include the following items: in parts per 100,000 by weight:—

1. Ammoniacal nitrogen.
2. Albuminoid nitrogen.
3. Total nitrogen.
4. Oxygen absorbed from strong permanganate in three minutes at 80°F. (3·94 grms. $KMnO_4$ per litre).
5. Oxygen absorbed from strong permanganate in four hours at 80°F.
6. Suspended solids.
7. Soluble solids.
8. Chlorine.

It is also desirable that the amount of dissolved oxygen taken up during the oxidation of the ammoniacal and organic matter of the sewage should be given.

The results of analysis would, of course, require to be properly interpreted; but as a rough guide, it may be taken that from the figure for 'oxygen absorbed from strong permanganate in 4 hours at 80°F.,' the strength of the sewage may be very roughly classified as follows:—

'Strong'	sewage	17–25	parts	per 100,000.
'Average'	,,	10–12	,,	,,
'Weak'	,,	7–8	,,	,,

In cases where the sewage cannot be analysed its strength should be estimated according to the water consumption, the flow per head, the kind of sewerage system, whether water-closets are in general use, the volume and nature of the trade waste, the amount of dilution by subsoil or surface water, &c.

Failing satisfactory evidence to the contrary, it will be desirable to assume that the sewage is 'strong' for the purpose of estimating the required capacity for the disposal works.

For the purpose of showing the *minimum* total cubic contents of filters required for treating three times the dry weather flow in different cases, the tables A and B have been prepared on the data given in the Commission's Report. Wherever possible, the figures are calculated from the data on pp. 117 and 118 of the Fifth Report, otherwise the calculations are based on the data in the tables between pp. 202 and 203.

The rates of filtration given by the Commission are rates which can generally be *doubled* in wet weather. Where it is proposed to deal with *three* times the dry-weather flow, the Commission say that it would generally only be necessary to provide 1½ times the capacity of filter required for the dry-weather flow (paragraph 293 of Report, 209). Hence the rates of filtration given by the Commission must be reduced by one-third to arrive at the basis for calculating the size of the filters for *three* times the dry-weather flow, and this reduction has been made in arriving at the figures in the tables.

TABLE A.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF PERCOLATING FILTERS.

Preliminary treatment	Strong sewage		Sewage of average strength		Weak sewage	
	Coarse or medium material	Fine material	Coarse or medium material	Fine material	Coarse or medium material	Fine material
Detritus tanks	15	*	25	*	40	*
Septic tanks	45 †	*	70	*	100	100
Settlement tanks (continuous flow) .	45 †	*	70	*	100	100
,, ,, (quiescent) . .	50 †	25	100	70	130	130
Precipitation tanks (continuous flow)	65	50	100	80	150	175
,, ,, (quiescent) .	100	65	130	130	170	200

Notes as to filtering material. (*a*) A filter may be regarded as '*coarse*' if the material will not pass through a 1-inch sieve; as '*medium*' if it will pass through a 1-inch but not through a ½-inch sieve; and as '*fine*' if it will pass through a ½-inch sieve.

(*b*) '*Coarse*' material will be desirable in all cases where the liquid to be treated contains much suspended matter.

(*c*) In the cases marked *, the use of fine material would not be desirable unless the circumstances were exceptional.

If '*medium*' sized material were used in the cases marked †, the figures should be reduced by about 10.

TABLE B.—CONSTANTS FOR CALCULATING THE MINIMUM CUBICAL CONTENTS OF CONTACT BEDS.

Preliminary treatment	Strong sewage			Sewage of average strength			Weak sewage		
	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact	Single contact	Double contact	Triple contact
Detritus tanks	—	—	25 *	—	25	†	—	38	†
Septic tanks	—	—	33	—	38	†	75 *	66 ‡	†
Settlement tanks (continuous flow)	—	—	33	—	38	†	75 *	66 ‡	†
,, ,, (quiescent) . .	—	—	44	—	50	†	100	†	†
Precipitation tanks (continuous flow)	—	33	†	—	50	†	133 ‡	†	†
,, ,, (quiescent) .	—	43	†	—	66 *	†	133 ‡	†	†

Notes. (*a*) The beds should not be less than 2 ft. 6 ins. nor more than 6 ft. in depth.

(*b*) The different series of beds, in double and triple contacts, should have equal cubic contents, failing any evidence to the contrary.

(*c*) Where a blank is left in the tables, the particular treatment indicated would only be desirable in exceptional circumstances, as the method would not generally be economical.

(*d*) In the cases marked thus †, the particular treatment indicated would only be necessary in exceptional circumstances (*i.e.* when an unusually good effluent is required).

(*e*) Where three times the d.w.f. has to be dealt with in wet weather, the individual beds, in the cases marked ‡, should be small (to facilitate rapid filling and emptying) or the total cubic contents of the filters should be increased.

(*f*) The average liquid capacity of a cubic yard of contact bed is about 50 gallons. There are no data in the Commissioners' report with regard to the cases marked thus *.

In order to ascertain the minimum total cubic contents of the filters required, divide the dry-weather flow by the *appropriate figure* (having regard to the strength of the sewage and the kind of treatment proposed) in the tables and the result will be the number of cubic yards which the filters should contain for treating up to three times the dry-weather flow, thus:—

Example 1. A 'strong' sewage is to be treated by means of '*septic tanks*' and '*percolating filters*,' of '*coarse*' material, and the dry-weather flow is 90,000 gallons. The appropriate figure in Table A is 45—then 90,000 gallons÷45=2000: the minimum total number of cubic yards which the filters should contain.

Example 2. An 'average' sewage is to be dealt with by means of '*quiescent settlement tanks*' and '*double-contact beds*,' and the dry-weather flow is 50,000 gallons—the appropriate figure in Table B is 50—then 50,000÷50=1000: the minimum total number of cubic yards which the filters should contain; and as in most cases the two series of beds would have the same cubic contents, there would be 500 cubic yards in the 'primary' beds and an equal number in the 'secondary' beds.

The definitions of the different classes of sewage and filtering materials must be regarded as being of an elastic nature, and it may sometimes be found desirable to use intermediate figures between those given in the tables in order to ascertain the required cubic contents of the filters.

In cases where a sufficient area [1] of suitable land is used for irrigating the filtrate, it will probably suffice if the total cubic contents of the filters is half that provided for by the tables, but where the filter capacity is so reduced it may be necessary in wet weather to restrict the flow to the filters to about 1½ times the dry-weather flow and to pass the remainder of tank liquor direct to the land.

Effluent tanks or filters. Where the effluent from filters is not irrigated on land, tanks (with a capacity equal to about two hours' dry-weather flow and with provision for removing sludge) or shallow straining filters, will in most cases be necessary for the purpose of preventing the suspended matters in the filtrate from passing into the river.

Sludge disposal. The disposal of the sludge resulting from the preliminary treatment of sewage is the *bête noir* of the sewage problem, especially in the case of large towns or cities not situated on or near the sea-board. For small works not situated in the near vicinity of dwelling-houses, land drying or lagooning is, as a rule, advisable, the dried sludge being disposed of to farmers or by digging it into the soil. For medium sized works, trenching in the ground is preferable, and for large inland works with a limited land area, preliminary treatment of the sludge by filter pressing is desirable before disposal to farmers, or on to land, or by burning with town refuse. At Harburg-on-Elbe and at Frankfort-on-the-Main, plants for sludge drying by centrifugals have been installed (Engineering, 1909), the dried sludge at the latter place being burned in a destructor in connection with the town refuse. At Oldham, Dr. Grossman has in course of erection a plant to recover grease and manufacture a manure from the sewage derived from a population of 147,000.

The principle on which Grossman's process is based is as follows:—The sludge is, in the first instance, dried in a special drying machine; then mixed with acid in order to liberate the fatty acids and heated in a distilling retort whilst superheated steam is passed over the mass. The superheated steam carries with it all the fatty matter contained in the sludge, and after being condensed by means of cold water, the grease collects at the top. The residue left in the retort is automatically discharged in the state of a fine, brown, odourless powder and possesses manurial properties.

At Bradford, where the sewage contains a considerable quantity of wool-scouring liquid, the recovery of the grease from the sewage has been so far successful that the return from the sale of the products more than meets the working expenses of the tank treatment. The sewage, after screening, is treated with sulphuric acid in such quantity that there is an excess equal to 10 parts H_2SO_4 per 100,000. The acid sewage is subsequently passed through settling tanks. The sludge is removed from the settling tanks into cast-iron vats, where a further quantity of sulphuric acid is added, and the temperature of the sludge is raised by steam to 100°. It is then run into steel rams and forced by compressed air into filter presses heated by steam, and the process of pressing is continued from 12 to 24 hours, hot sludge and steam being alternately admitted to the press. The pressed liquor, consisting of water and fat, is run into special vessels for the separation of the fat, after which the fat is boiled with acid and black oxide of manganese, in order to bring it into a marketable condition.

The amount of wet sludge produced in a year is about 100,000 tons. It contains about 80·15 p.c. of water, and 7·43 p.c. of grease, which is equivalent to 37·7 p.c. of grease on the dry matter.

The amount of pressed cake produced in a year is about 20,000 tons. This contains about 27 p.c. of water. Part of the pressed cake is used for fuel and is burnt in specially constructed brick furnaces; the fuel value is about 1*s.* 6*d.* per ton. Part is sold to farmers at 3*s.* 6*d.* per ton on rail at the works. Another portion is disintegrated and sold as manure at 5*s.* 6*d.* per ton, whilst 6*s.* 3*d.* per ton is obtained for the driest portion of the disintegrated pressed cake.

Tests for sewage effluents in relation to standards. The Royal Commission (8th report) recommend a normal standard. This standard should apply to all sewage discharges into non-tidal waters, except where local circumstances are shown to justify a special standard. A normal standard effluent should not contain more than 3 parts of suspended matter per 100,000, and that, including its suspended matters, it should not take up more than 2 parts of dissolved oxygen per 100,000 in 5 days at 65° Fahr.

A claim for a relaxed standard may be entertained under the following conditions:—

(*a*) When it can be shown that the particular river water is of such quality and volume that, when mixed with a sewage or sewage liquor of known or calculated strength and volume, it does not take up more than 0·4 part per 100,000 of dissolved oxygen in 5 days; and

(*b*) When there is reason to suppose, or when it can be shown that the river will receive no further pollution until it has recovered itself so far as not to take up in 5 days an amount of dissolved oxygen much in excess of that which it took up before receiving the first discharge.

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[1] Viz. from 3000 to 30,000 gallons (dry-weather flow) per acre per twenty-four hours according to the quality of the land.

SEWAGE FATS. Sewage water (waste water from households, abattoirs, &c.) contains fatty matter in the form of soap, unsaponified fat, free fatty acids, and unsaponifiable matter. As sewage water is of an extremely putrescible nature, sanitary conditions require its immediate removal (from houses, &c.) and both rapid and careful treatment at the sewage works, so as to render the effluent innocuous in a manner best adapted to local conditions.

Up to about a decade ago no attempt had been made to recover the fatty matter. In the precipitation processes, which are employed to a great extent, the fatty matter is deliberately wasted, and one of the chief features of the biological ('digestive') processes is to destroy the fat as completely as possible by making it serve as a foodstuff to the bacteria which digest the fatty matter contained in raw sewage.

During the last decade, however, endeavours have been made, on a large scale, to recover the fatty matter contained in the sewage. Most of the recovery processes are designed on the lines of the methods practised in the wool, cotton, and silk industries and especially in the recovery of wool grease from wool scourers' suds. (For further details of these processes, *cp.* Lewkowitsch, Chem. Tech. iii. 366.)

The composition of 'sewage fats' must vary with the localities whence they originate. Owing to the exceedingly favourable conditions for the micro-organisms thriving in raw sewage, the bulk of the neutral fat discharged into the sewage is hydrolysed; therefore 'sewage fats' are characterised by large proportions of free fatty acids. The amount of unsaponifiable matter is also considerable. The nature of the unsaponifiable matter has not yet been investigated. Probably it consists to a large extent of coprosterol, which forms an important constituent of excrementitious matter.

Judging from the composition of sewage fats it is evident that the products cannot pay the expenses of the process, unless, indeed, the recovery of the fat form an integral part of the sewage disposal process. J. L.

SHALE OIL *v.* Paraffin.

SHANGHAI OIL. A variety of colza oil *v.* Oils, Fixed, and fats.

SHEA BUTTER *v.* Bassia oils.

SHELLAC *v.* Resins.

SIDERITE *v.* Chalybite.

SIEMENS STEEL *v.* Iron.

SIENNA *v.* Pigments.

SILBEROL *v.* Synthetic drugs.

SILEX, SILICA, *v.* Silicon.

SILICATE COLOURS *v.* Paints and Pigments.

SILICATE PAINTS *v.* Paints and Pigments.

SILICIOUS CEMENTS *v.* Cements.

SILICON. Sym. Si. At. wt. 28·3. Silicon is not found in the free state in nature, but occurs abundantly as silica and metallic silicates. It is known in the following modifications:—

1. **Amorphous silicon,** first obtained by Berzelius (1823) by heating dry potassium or sodium silico-fluoride with an equal weight of potassium or sodium respectively.

By passing the vapour of silicon chloride over potassium or sodium, heated in a porcelain boat, or over heated aluminium (Hautefeuille and Perrey, Compt. rend. 100, 1220).

By passing silicon fluoride over metallic sodium at 400°–500°, and heating the powdered product with sufficient sodium to decompose any sodium silico-fluoride formed, and with aluminium in sufficient quantity to form an alloy of not more than 16 p.c. Si. The residue after treating with hydrochloric acid, is lead grey in colour, and contains 3–4 p.c. of silica. On extracting with hydrofluoric acid, brown amorphous silicon is obtained in a very reactive form (Hempel and v. Haasy, Zeitsch. anorg. Chem. 1900, 23, 32).

By heating magnesium powder and silica in the requisite proportions in presence of magnesia to moderate the action. The product is heated successively with dilute hydrochloric and sulphuric acids, then treated two or three times alternately with hydrofluoric and sulphuric acids, and finally with hydrochloric acid. Thus obtained, it is a maroon-coloured powder, containing only 0·4–1 p.c. impurity. Aluminium may be used instead of magnesium (Vigouroux, Compt. rend. 1895, 120, 94, 1161). If kieselguhr or precipitated silica is used, reaction takes place with aluminium in the cold (Weston and Ellis, Trans. Faraday Soc. 1908, 3, 170).

By sparking liquid silicon hydride (Moissan and Smiles, Compt. rend. 1902, 134, 1552).

By electrolysis of a fused mixture of potassium fluoride and silicofluoride.

For other electrolytic methods, *v.* Gore (Chem. News, 50, 113), Warren (*ibid.* 57, 54), Hampe (Chem. Zeit. 12, 841).

It is a brown or maroon-coloured powder, sp.gr. 2·35 at 15°; readily fuses and volatilises in the electric furnace, dissolves in many molten metals, readily absorbs gases and water vapour, which can only be expelled at red heat; not attacked by iodine, combines with bromine at 500°, chlorine at 450°, and with fluorine at ordinary temperatures with incandescence; oxidises superficially in air, burns in oxygen at 400°, combines with nitrogen at 1000°, and becomes incandescent in sulphur vapour at 600°; halogen acids attack it at dull red heat, but concentrated hydrofluoric acid at 100° has no action; reduces carbon dioxide to carbon monoxide at 800° (Vigouroux, Compt. rend. 120, 367).

It is attacked by hot water in glass vessels, which explains the poor yield with many workers, and when heated with hydrofluoric acid becomes much more reactive, being violently attacked by concentrated nitric acid (Wilke, Dörfurt Festschrift Otto Wallach, 1909, 671).

It reduces many metallic fluorides and oxides below red heat. As prepared by sparking silicon hydride it is capable of reducing salts in solution.

2. **Graphitoidal silicon.** By strongly heating amorphous silicon in a platinum crucible (Berzelius). By electrolysis of sodium aluminium chloride and extraction with hydrochloric acid (Deville). By strongly heating a mixture of aluminium with 20 to 40 times its weight of potassium silicofluoride; after successive treatment of the product with hydrochloric and hydrofluoric acids, graphitoidal silicon remains in the form of hexagonal tables with curved edges (Wöhler, Compt. rend. 42, 48).

By fusing the product obtained on heating a mixture of finely powdered sand and magnesium in a test-tube, with aluminium and cryolite. On treatment with water and acids, black glistening spangles of graphitoidal silicon remain (Hyde, J. Amer. Chem. Soc. 1899, 21, 663).

Also by fusing aluminium (1 part) with glass free from lead (5 parts) and cryolite (10 parts), and treating successively with hydrochloric and hydrofluoric acids; sp.gr. 2·49. Unaltered in oxygen at white heat, but burns brilliantly when heated to redness with potassium carbonate, although only at white heat with the chlorate or nitrate. Unattacked by acids, except by a mixture of nitric and hydrofluoric acids. Soluble in strong potash or soda; combines with chlorine at red heat, and with fluorine at the ordinary temperature. It reduces many metallic oxides, in some cases with explosive violence (Warren, Chem. News, 64, 75).

3. **Crystalline or adamantine silicon** is obtained according to Deville on heating amorphous silicon in a platinum crucible lined with lime to a temperature between the melting-points of steel and cast-iron, in dark, steely grey globules, sometimes yielding double six-sided pyramids (Ann. Chim. Phys. [3] 49, 68).

When silicon chloride vapour is passed over aluminium fused in an atmosphere of hydrogen, a portion of the aluminium is volatilised as chloride, and the remainder becomes saturated with silicon. At the point of saturation the excess of silicon separates in large needles of dark iron-grey colour, reddish by reflected light, and iridescent. The form is derived from a rhombic octahedron, and the crystals often exhibit curved faces. They are capable of cutting glass.

By heating to redness in a clay crucible, a mixture of potassium silico-fluoride (3 parts), sodium (1 part), and zinc (4 parts). The zinc is removed by fusing and then by successive treatment with hydrochloric and boiling nitric acids, leaving the crystalline silicon in long needles (Deville and Caron, Ann. Chim. Phys. [3] 63, 26; *ibid.* [3] 67, 441; Robins, Chem. News, 5, 102); *v.* also Kühne (D. R. P. 147871); Hollemann (Proc. K. Akad. Wetensch. Amsterdam, 1904, 7, 189).

It is most conveniently obtained by the action of aluminium upon potassium silico-fluoride. The product, purified in the usual way, still contains traces of iron, and Vigouroux (Bull. Soc. chim. 1907, [iv.] 1, 16) has obtained it in a pure condition by digesting for some time with diluted hydrofluoric acid (1:1) in a platinum vessel, and then with concentrated sulphuric acid, these processes being repeated until no residue is left on evaporation with a mixture of nitric and hydrofluoric acids.

It is less reactive than amorphous silicon, although by rapidly heating in oxygen it may be made to take fire at 400°. It is also attacked, if finely divided, by boiling water, but not in fused quartz or platinum vessels (Moissan and Siemens, Compt. rend. 1904, 138, 939).

A *new modification* is described by Moissan and Siemens (*ibid.* 1904, 138, 1299). It is obtained mixed with the ordinary crystalline form from a solution of silicon in molten silver, in which it is very soluble (41·66 p.c. at 1470°, 9·22 p.c. at 970°). Yield is 99 p.c. from a 2 p.c. solution, decreasing with increasing amounts of silicon. It is readily attacked by hydrofluoric acid, thus differing from other modifications: sp.gr. 2·42, *v.* also Warren (Chem. News, 67, 136).

Silicon as such has received no important commercial application, but Le Roy (Compt. rend. 1898, 126, 244) recommends it for electrical heating in place of metallic and carbon resistances. A rod, 10 cms. long and 40 sq. mm. cross section, has a resistance of 200 ohms, that of a similar carbon rod being 0·15 ohms.

Silicon steel *v.* Iron.

For the spectra of silicon and its compounds, *v.* Wesendonck (Wied. Ann. 21, 427); Hartley (Chem. Soc. Trans, 1883, 397; Proc. Roy. Soc. 1901, 68, 109); Lunt (*ibid.* 1900, 66, 44); Lockyer (*ibid.* 1899, 65, 449); Pollock and Leonard (Sci. Proc. Roy. Dubl. Soc. 1907, [ii.] 17, 217); Dufour (Compt. rend. 1908, 146, 810); De Gramont and de Watteville (*ibid.* 1908, 147, 239).

The refraction equivalent of silicon is 7·4 (Gladstone, Chem. Soc. Trans. 1891, 299).

For its refraction and dispersion in combination, *v.* Abati (Gazz. chim. ital. 1897, 27, ii. 437). Sp.ht. 1·36 at −39·8°; 2·029 at 232·4° (Weber, Ann. Chim. Phys. [5] viii. 132). Morphotropic relations between carbon and silicon compounds (*v.* Jerusalem, Chem. Soc. Trans. 1910, 2190).

Estimation v. Analysis.

Silica, *silicic anhydride*, SiO_2, occurs abundantly in nature, in pure or nearly pure condition, the crystalline varieties including quartz, chalcedony, hornstone, jasper, tridymite, quartzine and lutecite, while in the amorphous state it is found in the various forms of opal. In impure condition it occurs as sand and flint, and it enters largely into the constitution of sandstones, felspars, and many other rocks.

Silica may be artificially prepared:—

1. By burning silicon in air or oxygen.
2. By the action of water upon the tetrahalides of silicon, the gelatinous hydrate obtained yielding silica on ignition as a very light, white powder.
3. By the decomposition of silicates.

Many of these are decomposed by acids, and the silica so obtained from them often resembles the mineral from which it is derived. Chrysolite on boiling with dilute acids yields silica which is brilliantly white and fibrous like the mineral. Even after heating to redness it still retains the flexibility of silk. Serpentines and magnesian silicates generally, yield fibrous and not gelatinous silica (Terreil, Compt. rend. 100, 251; *v.* also Gorgeu, *ibid.* 98, 1281). Silicates which are not attacked by acids may be decomposed by fusion with sodium and potassium carbonates, the silica being rendered insoluble by subsequent evaporation with hydrochloric acid.

Properties. The physical properties of natural silica vary somewhat with the different forms. Crystalline varieties have sp.gr. 2·3–2·8 (quartz = 2·64–2·67; tridymite = 2·28–2·43) and amorphous forms 1·9–2·3 (quartz glass, 2·213; Day and Shepherd, J. Amer. Chem. Soc. 1906, 28, 1089). Other physical constants for the natural varieties will be found under the various minerals.

In presence of fused chlorides, quartz glass crystallises as quartz below 760°, and as tridymite above 800°, while at the lower temperature tridymite changes to quartz, the change being enantiomorphic (Day and Shepherd, *l.c.*). The crystalline forms can also be obtained artificially from solution (Chrustschoff, Jahrb. Min. 1887, 1 Mem. 205; Königsberger and Muller, Centr. Min. 1906, 657, 728).

Amorphous silica prepared by fusion in the electric furnace has a mean coefficient of expansion of 0·0000007 between 0° and 1000° (Le Chatelier, Compt. rend. 1900, 130, 1703).

Its m.p. is about 1600°. It can be quickly volatilised in an electric arc of 360 ampères and 70 volts, and in this way may be separated from zirconia or thoria (Moissan, Compt. rend. 116, 1428; *v.* also Cramer, Zeitsch. angew. Chem. 1892, 484; Schützenberger, Compt. rend. 116, 1230).

Silica is a catalyst of alcohols (Senderens, Compt. rend. 1908, 146, 125). With the moderately calcined substance, ethylenes are obtained almost exclusively, the yield from ethyl alcohol at 280° being 99·5 p.c.

Heat of formation 190·985 cal. (Mixter, Amer. J. Sci. 1907, [iv.] 24, 130).

For crystallography of polymorphous forms of silica, *see* Barlow and Pope (Chem. Soc. Trans. 1908, 1554). Silica is insoluble in microcosmic salt. It is insoluble in all acids except hydrofluoric acid which decomposes it, forming water and silicon fluoride. It dissolves fairly readily in caustic soda, hyalite dissolving more slowly than the other varieties; quartz requires boiling or increased pressure. Amorphous silica in fine powder and gelatinous silica dissolve partially in alkali carbonate solutions, the silica being deposited in gelatinous form on cooling. It is readily converted into alkali silicate by fusion with alkali hydroxide or carbonate. It is insoluble in water, but is distinctly hygroscopic, this property decreasing with the degree of calcination (Souchy, Bull. Soc. chim. [2] 13, 509).

With PCl_3 and PCl_5 at red heat, $SiCl_4$ is produced, as is the case when chlorine is passed over a mixture of the oxide with charcoal at red heat. It is not affected, however, by CCl_4.

It is reduced by metals (*v. Silicon, Preparation of*), and by carbon in the electric furnace (Moissan, Compt. rend. 1895, 120, 1393). For its action upon alkaline haloid salts, *v.* Gorgeu, (Compt. rend. 102, 1164).

It gradually absorbs lime from lime-water, forming $3SiO_2{\cdot}4CaO$ (Laudrin, *ibid.* 96, 841). It is dissolved in small quantities by ammonia (Souchay, Zeitsch. anal. Chem. 1872, 182). Its use has been advocated for decolourising oils (Stern, Warsaw, Eng. Pat. 1890, 7142). While not an essential constituent of plant food it plays a definite part in the nutrition of cereals (Hall and Morison, Proc. Roy. Soc. 1906, 77 B, 455).

Fused silica-ware is now extensively employed in laboratory and technological operations. The first attempts to utilise silica in this way were made by Gaudin in 1839 (Compt. rend. 8, 678, 711), who succeeded in spinning threads of fused silica by hand, and also made small pellets which he found to be inactive to polarised light. The production of capillary tubes and spirals was described by Gautier in 1869 and exhibited at the Paris Exhibition in 1878. In 1887, Boys (Phil. Mag. 1887, 489) produced quartz fibres, the torsion of which he applied to the measurement of small forces; he also produced small tubes and bulbs. In 1901, Shenstone (Proc. Roy. Inst. 1901, 525) demonstrated a method of producing before the oxy-coalgas blowpipe flame, tubes, bulbs, and other apparatus suitable for use in scientific work.

Physical properties. Sp.gr. 2·21 (*v.* Day and Shepherd, *l.c.*). Coefficient of expansion $44{\cdot}9 \times 10^{-8}$ (Minchin, Phys. Review, 1907; *v.* also Le Chatelier, *l.c.*; Kaye, Phil. Mag. 1910, 20, 718). It expands on cooling from 1500° to 1200° (Le Chatelier, *l.c.*). Refractive index for D line 1·4584772 (Shenstone and Gifford, Proc. Roy. Soc. 1904, 201).

Its m.p. is not well defined; at the m.p. of platinum it is appreciably soft, but not workable. It probably commences to soften at about 1500°. It vapourises freely in the electric arc, but at its b.p. is still a very viscous liquid, nor does its fluidity increase on raising the b.p. by increasing the pressure.

In consequence of its low coefficient of expansion it possesses to a remarkable degree the power of resisting sudden changes of temperature. Boys has shown it to be an excellent insulator, even in an atmosphere saturated with moisture.

It is permeable to gases at high temperatures (Villard, Compt. rend. 130, 1752; Berthelot, *ibid.* 140, 821).

PHYSICAL PROPERTIES OF QUARTZ FIBRES.

Diam. of thread 0·00175 cm.; tenacity	$8{\cdot}0\times10^{9}$	C.G.S.
„ „ 0·00048 „ „	$11{\cdot}5\times19^{9}$	„
Young's modulus at 20°C. „	$5{\cdot}6\times10^{9}$	„
Modulus of simple rigidity at 20°C. „	$2{\cdot}65\times10^{9}$	„
„ incompressibility „ „	$1{\cdot}4\times10^{9}$	„
„ torsion „ „	$3{\cdot}7\times10^{9}$	„

(Threlfall, Laboratory Arts, 218).

Chemical properties. Fused silica is very resistant, being attacked only by fused alkalis, hydrofluoric acid, and to a small extent by phosphoric acid. Even with hydrofluoric acid no etching is produced if the silica be pure, the material dissolving away so as to leave a smooth surface. Certain metallic oxides, such as those of lead and copper attack silica if heated in contact with it.

Fused silica, on account of its slow devitrification which commences at 1200°, should not be used for continuous work at higher temperatures, though quite satisfactory for intermittent work, *i.e.* pyrometric measurements. It is used as a standard of length at the National Physical Laboratory (Kaye, Proc. Roy. Soc. 1911, A, 85, 430) and in mercurial thermometry. Silica finds further commercial application in the manufacture of artificial stone and hydraulic cements. Kieselguhr is employed in making dynamite, ultramarine, water-glass enamels and glazes, also as a polishing agent, a filling material for paper, soap, and other articles, and as a medium in the filtration of water (*v.* Nordtmeyer, Chem. Zentr. 1891, 932).

Silicon monoxide SiO is described by Potter (D. R. P. 189833) as a voluminous brown powder obtained by heating silica electrically in an inert atmosphere with sufficient carbon or carbon silicide to remove one half of the oxygen;

sp.gr. 2·24. Much less readily soluble in hydrofluoric acid than silica but more readily soluble in potassium hydroxide. It is patented as a pigment under the name of 'monox' (Eng. Pat. 1279, 1906).

Silicic acids. Four silicic acids are usually stated to exist, viz.:

Orthosilicic acid,	H_4SiO_4
Metasilicic acid,	H_2SiO_3
Polysilicic acid,	$H_4Si_3O_8$
Disilicic acid,	$H_2Si_2O_5$.

Polysilicic acid may be regarded as composed of metasilicic and disilicic acids: $H_2Si_2O_5+H_2SiO_3=H_4Si_3O_8$ (Groth).

On the other hand, orthosilicic acid and polysilicic acids may combine together to form metasilicic acid: $H_4SiO_4+H_4Si_3O_3=4H_2SiO_3$; and disilicic acid may be regarded as polysilicic acid from which orthosilicic acid has been abstracted: $3H_4Si_3O_8-H_4SiO_4=4H_2Si_2O_5$ (Becker, Am. S. 38, 154).

Considerable difference of opinion still exists as to the actual existence of definite hydrates of silica, Chatelier (Compt. rend. 1908, 147, 660) holding that the water is not chemically combined. The existence of *metasilicic acid* H_2SiO_3 would, however, appear to be proved. According to Butureanu (Ann. Sci. Univ. Jassy, 1901, 1, 319) it is obtained as a white powder by dehydrating gelatinous silicic acid, prepared by adding mineral acid to an alkali silicate solution, with 90 p.c. alcohol.

Orthosilicic acid H_4SiO_4 is said to be obtained by washing the precipitated silicic acid prepared by the action of silicon fluoride upon water, with benzene or ether, and rapidly drying between bibulous paper (Norton and Roth, J. Amer. Chem. Soc. 1897, 19, 832) and also by the action of silicon chloride upon water (Tschermak, Zeitsch. anorg. Chem. 1909, 63, 230).

Tschermak, in the course of his work upon the constitution of silicates, claims to have proved the existence of other hydrates, by the breaks in the dehydration curves of the gels obtained by decomposing the silicates with hydrochloric acid. His conclusions are based on the assumption that the acid set free is the acid from which the salt is formed, and that the process of drying takes place in two distinct stages—evaporation of excess of water, followed by dehydration of the acid (Centr. Min. 1908, 129, 225; Zeitsch. anorg. Chem. 1910, 66, 199). The method is adversely criticised by Mügge (Centr. Min. 1908, 129, 325), van Bemmelen (Zeitsch. anorg. Chem. 1908, 59, 225; 1909, 62, 1) and Serra (Atti. R. Accad. Lincei, 1910, [v.] 19, 1, 202). The last-named finds that the temperature and concentration of the hydrochloric acid, and the temperature at which the silicic acid is dried, influence the result.

The various hydrates described by Merz (J. pr. Chem. 99, 177), Gottlieb (*ibid.* [2] 6, 185), and Langlois (Chem. Soc. Trans. 1858, 140) are probably not definite compounds (Carnelly and Walker, *ibid.* 1888, 1, 66, 80).

Gelatinous silica (hydrogel form) is also obtained by the action upon alkali silicate solutions of oxalic (Monier, Compt. rend. 86, 1318), sulphurous (Doveri, J. pr. Chem. 42, 194), carbonic, and boric acids (Vogel, Jahresber. 1870, 295), and the physical properties vary with the conditions of precipitation, particularly its solubility in water. According to Jordis (Zeitsch. Electrochem. 1905, 11, 835; Chem. Zentr. 1907, 1, 392), the hydrogel produced with sodium silicate and hydrochloric acid may be soaked in water until finally neither hydrogel nor washings give a reaction for chlorine. If then extracted with hot water the washings again give a strong reaction for chlorine. Sodium is also present, and Jordis considers that these elements are not present in the form of sodium chloride.

For the ultramicroscopic study of silicic gels, *v.* Zsigmondy (Zeitsch. anorg. Chem. 1911, 71, 356).

Silicic acid is a very weak acid. In its colloidal form it may be detected by its solubility in boiling alkali paratungstate solutions, forming silico-tungstates. The potassium salt in presence of sodium chloride gives a crystalline precipitate with 5 p.c. cæsium chloride solution (Hermann, Zeitsch. anal. Chem. 1907, 46, 318). Silica jelly is an excellent culture medium for micro-organisms (Kühne, Zeitsch. Biol. 27, 172). It also finds application in sugar refining (Vibrans, Chem. Zeit. 1880, 426).

Soluble silicic acid (hydrosol) was the subject of extensive researches by Graham, upon the results of which he laid the foundations of colloid chemistry. If a dilute solution of an alkali silicate be poured into large excess of hydrochloric acid, the silicic acid remains in solution, and may be purified by dialysis by means of parchment paper, and concentrated by evaporation to a silicic acid content of 18 p.c. The solution is tasteless and limpid, with a slightly acid reaction, and readily coagulates. Hydrochloric acid and small quantities of potash or soda retard the coagulation. Evaporated at 15° *in vacuô* the silica remains as a transparent glassy, lustrous hydrate containing 22 p.c. of water (Chem. Soc. Trans. 1861, 204; *v.* also Church, J. pr. Chem. 89, 187; Doveri, *l.c.*; Kühn, J. pr. Chem. 59, 1).

It may also be obtained by hydrolysis of methyl silicate (8 grms.) with water (200 grms.) at boiling temperature, and evaporating to two-thirds its bulk to expel methyl alcohol, the solution so obtained containing 2·26 p.c. of SiO_2, and differing from Graham's solution in that it is not coagulated by carbon dioxide (Grimaux, Compt. rend. 98, 1434).

The coagulating effect of electrolytes has been studied by Pappada and Sadowski (Zeitsch. Chem. Ind. Kolloide, 1910, 6, 292), who find the effects of different ions to be approximately proportional to their rates of diffusion.

Dialysed silicic acid containing the least trace of hydrochloric acid, gives no luminous beam when optically examined, even on evaporation, showing that the molecular aggregates are not sufficiently large to scatter light. If completely dialysed, the gradual condensation is indicated by a feebly luminous beam, slowly increasing in intensity (Picton and Linder, Chem. Soc. Trans. 1892, 154).

Mylius and Groschuff (Ber. 1906, 39, 116) find the molecular weight of soluble silica when freshly prepared (α silicic acid) to be about 155. It is not precipitated by egg-albumen, methylene blue, or sodium hydroxide, but slowly changes—rapidly on warming—to the β-silicic acid, which is also soluble, but is precipitated by these substances, and according to Sabanéeff (J. Russ. Phys. Chem. Soc. 21, 515) has a molecular weight of not less than 48,000. Heat of coagulation +11·8 cal. (Wiedermann and Lüdeking, Ann. Chim. Phys. [2] 25, 145).

Alkosol and alkogel, and corresponding glycerol compounds with silicic acid, are also described by Graham (J. pr. Chem. 94, 347).

Esters corresponding to the acids, H_2SiO_3 and H_4SiO_4, are also known.

Thiosilicic acid is only known in the form of its sodium salt, which is obtained by fusing together pure sodium sulphide and silicon disulphide. Na_2SiS_3 is a brownish-black mass decomposed by water and acids (Hempel and Haasy, Zeitsch. anorg. Chem. 1900, 23, 32).

COMPLEX ACIDS CONTAINING SILICON.

The chief of these are *silico-stannic*, *silico-titanic* (Bourgeois, Compt. rend. 104, 231), *silico-zirconic* (Ouvrard, *ibid.* 113, 82), *silico-molybdic* (Asch, Zeitsch. anorg. Chem. 1901, 28, 273; Copaux, Ann. Chim. Phys. 1906, [viii.] 7, 118; Bull. Soc. franc. Min. 1907, 30, 292), *nitro-silicic* (Rousseau and Tite, Compt. rend. 114, 294), and *silico-tungstic* (Copaux, Bull. Soc. chim. 1908, [iv.] 3, 101). Sodium silico-tungstate is a good mordant for basic aniline colours (Scheurer, Leipziger Farber- und Lengdr. Zeit. 1900, 49, [6] 60). The free acid or its sodium salt in 5 p.c. solution is said to be the best general precipitant for alkaloids, forming precipitates which are practically insoluble in cold water, and from which the alkaloid is at once regenerated by dilute soda or ammonia (Bertrand, Compt. rend. 1899, 128, 742).

Silico-oxalic acid $(HO{\cdot}OSi{\cdot}SiO{\cdot}OH)_x$ is a white solid obtained by exposing pure Si_2Cl_6 in a platinum dish cooled in ice, till solid, and then over lime until all hydrochloric acid is removed. When heated in a test-tube it decomposes violently with feeble detonation, and also explodes with friction. With potassium hydroxide hydrogen is evolved

$$H_2Si_2O_4+4KOH=2K_2SiO_3+2H_2O+H_2.$$

It reduces $KMnO_4$ in the cold (Friedel and Ladenburg, Annalen, 203, 250; Gatterman and Weinlig, Ber. 27, 1943; *v.* also Troost and Hautefeuille, J. pr. Chem. [2] 4, 302).

Silico-mesoxalic acid

$$(SiOOH{\cdot}Si(OH)_2SiOOH)_x$$

is similarly obtained from Si_3Cl_8, but is more violently explosive, and has stronger reducing properties than the silico-oxalic acid. When dry it is extremely unstable, often decomposing spontaneously and becoming incandescent (Gattermann and Ellery, Ber. 32, 1114).

Silico-formic anhydride (*v.* under SILICO-CHLOROFORM).

Silicones. These oxygen-hydrogen compounds of silicon are produced by the action of aqueous hydrochloric acid on metallic silicides.

Chryseone or *silicone* $Si_4H_4O_3$ is described by Wöhler as obtained in orange-coloured laminæ by digesting calcium silicide with concentrated hydrochloric acid in absence of light. On exposure it becomes snow-white in colour, changing to *leucone* $Si_3H_4O_5$. If dilute acid is used, the *substance*, $Si_4H_8O_5$, is obtained (Wöhler and Buff, Annalen, 104, 101; Wöhler, *ibid.* 127, 257). Hönigschmidt (Monatsh. 1909, 30, 509) assigns to silicone the formula $Si_3H_3O_2$ from the amount of hydrogen evolved when heated in a vacuum. The residue has the composition Si_3O_2. Leucone gives no definite result by this method, but leaves a residue approximating in composition to Si_3O_4. Similar bodies of indefinite composition are obtained from magnesium and other silicides (Geuther, J. pr. Chem. 95, 424; Winckler, Ber. 23, 2642). They are probably mixtures of silicoformic anhydride and silico-oxalic acid (Boudouard, Compt. rend. 1906, 142, 1528).

SILICON AND HYDROGEN.

Silicon hydride, *silicomethane*, SiH_4, was first obtained, mixed with hydrogen, by Wöhler and Buff (Annalen, 102, 128; 103, 218; 104, 94; 107, 112; Jahresber. 1857, 166; 1858, 142), (*a*) by electrolysis of sodium or other metallic chloride using as the positive pole an alloy of aluminium and silicon, at which the spontaneously inflammable gas escapes; (*b*) by the action of hydrochloric acid on magnesium silicide and other silicides.

So obtained by Wöhler and Buff it is a colourless, spontaneously inflammable gas, insoluble in de-aërated water, but decomposed over water containing air. SiH_4 may be obtained by direct synthesis from its elements. Silicon heated above its melting-point in hydrogen yields small quantities of SiH_4 (Dufour, Ann. Chim. Phys. 1906, [viii.] 9, 433).

The crude gas from magnesium silicide usually consists of about 95 p.c. hydrogen. On fractionating the gas by means of liquid air, Moissan and Smiles obtained a fraction boiling at about 52°, spontaneously inflammable, and of density approximately agreeing with the formula Si_2H_6 (Compt. rend. 1902, 134, 569).

Subsequently, Lebeau (*ibid.* 1909, 148, 13) obtained by this method SiH_4 and Si_2H_6 in the pure state, the latter of the calculated density and of b.p. $-7°$, and in addition a colourless liquid exploding violently with oxygen, and burning with a bright flame. This is probably Si_2H_4, although too reactive to allow of accurate analysis, and is probably the cause of the spontaneous inflammability of the crude gas. Finally, a white solid was obtained in small quantity, turning brown in air, presumably a solid hydride.

Silico-methane is obtained in the pure state by the decomposition of tri-ethyl silico ortho-formate in contact with sodium, on warming. The action of the sodium has not been explained (Friedel and Ladenburg, Bull. Soc. chim. [ii.] 7, 322).

$$4SiH(OC_2H_5)_3=SiH_4+3Si(OC_2H_5)_4.$$

According to Adwentowski and Drozdowski (Bull. Acad. Sci. Cracow, 1911, A, 330–344) this method only yields the pure gas after repeated fractionation. It is not spontaneously inflammable, except when gently heated under reduced pressure, or mixed with hydrogen. A hot knife-blade is sufficient to inflame the bubbles of gas as they rise over mercury, and the mercury becomes sufficiently heated to set fire to the succeeding bubbles.

It is decomposed by potassium hydroxide.

$$SiH_4+2KOH+H_2O=K_2SiO_3+4H_2.$$

1 litre at N.T.P. weighs 1·4538 grams; crit. temp. −35° C.; crit. press. 47·8 atmos.; b.p. −116°/74° mm. (Adwentowski and Drozdowski, *l.c.*) Heat of formation 24·8 cals. (Ogier, Compt. rend. 88, 911). Heat of combustion 324·3 cals.

The impure gas burns with formation of silica, and silicon is deposited when the flame plays on a porcelain basin.

It forms with copper and silver solutions the corresponding silicide, and precipitates metallic palladium from solution, but is without action on lead acetate or platinum chloride. It is decomposed by the electric discharge into hydrogen and a yellow solid (Ogier, Compt. rend. 89, 1068).

In addition to the *silico-ethane* and *silico-ethylene* already mentioned, *silico-acetylene* $(Si_2H_2)_x$ has been described by Bradley (Chem. News, 82, 149) as a yellow crystalline non-explosive compound obtained by treating the copper silicide $CuSi_2$ (*v.* however under *Metallic Silicides*) and the calcium silicide $CaSi_2$ (*q.v.*) with acids.

Silicon and Fluorine.

Silicon fluoride SiF_4 was first obtained by Scheele in 1771. It is produced by the action of hydrofluoric acid or concentrated sulphuric acid and a metallic fluoride, upon silica or silicates. Further, by strongly heating fluorspar with silica, or a mixture of clay and carbon as well as by direct synthesis (*v.* also under $SiHF_3$).

It is most conveniently prepared by treating a mixture of one part fine dry sand or glass powder and one part powdered fluorspar with six parts concentrated sulphuric acid, the gas being collected over mercury.

It is a colourless gas with a suffocating smell, and fumes strongly in air. It is not inflammable. It solidifies at −102° (Olzewski, Monatsh. 5, 127) and evaporates without fusion. Under two atmospheres pressure it solidifies without liquefying at −97°, and then melts at −77°, and boils at −65° under 1810 mm. Its critical temperature is −1·5° and its critical pressure 50 atmospheres. These constants are identical for both the synthetic product, and that obtained by the usual method (Moissan, Compt. rend. 1904, 139, 711).

Its spectrum contains characteristic blue bands which are absent from the silicon hydride spectrum (Wesendonck, Wied. Ann. 21, 427; *v.* also Dufour, Compt. rend. 1908, 146, 810).

It is decomposed by continued passage of the electric spark, with separation of silicon (Troost and Hautefeuille, Compt. rend. 43, 443).

It is readily absorbed in large quantities by water, being at the same time decomposed into silicic and hydrofluosilicic acids

$$3SiF_4+2H_2O=2H_2SiF_6+SiO_2.$$

It is not, however, decomposed by steam above 150° (Hautefeuille), and Guntz (Ann. Chim. Phys. [vi.] 3, 1) shows from the thermal equation

$$\begin{aligned}&SiF_4(\text{gas})+2(H_2O)(\text{gas})\\&\quad=2HF(\text{gas})+SiO_2(\text{sol.})=-25{\cdot}8\text{ cal.}\end{aligned}$$

that the latter action can only take place provided the temperature is sufficiently high to prevent the secondary action, viz. combination of hydrofluoric acid with water and formation of hydrofluosilicic acid, which develops heat sufficient to compensate this absorption.

The heat of formation of silicon fluoride is 269·4 cal.

Aqueous alkalis and alkaline earths decompose it, precipitating part of the silica and forming a fluosilicate of the metal, as is the case with potash, or precipitating the whole of the silica and forming a metallic fluoride, as is the case with soda.

Many anhydrous metallic oxides absorb silicon fluoride, becoming hot, and sometimes taking fire.

Potassium and sodium do not react until melted, when they blacken and burn with a dark-red flame, yielding a dark-brown brittle mass (Gay-Lussac and Thénard, Ann. Chim. Phys. 69, 204).

Silicon fluoride combines with twice its volume of ammonia gas, forming a volatile crystalline compound $(2NH_3)SiF_4$, which is decomposed by water in the following manner:

$$2((NH_3)_2SiF_4)+2H_2O=2NH_4F+(NH_4)_2SiF_6+SiO_2$$

(J. Davy). It is absorbed by absolute alcohol forming fluosilicic alcohol, a mixture of tetrethylic silicate and hydrofluosilicic acid (Knop and Wolf, Chem. Zentr. 1861, 82).

Aniline and a large number of other amines readily react with SiF_4 (Comey and Jackson, Ber. 21, 613; Comey and Smith, *ibid.* 21, 893c). Phosphine combines at −22° and 50 atmospheres pressure to give a white crystalline solid of formula $3SiF_4{\cdot}2PH_3$ (Besson, Compt. rend. 110, 80).

Silicon subfluoride, said to be obtained by passing the tetrafluoride over silicon heated nearly to the softening point of porcelain (Troost and Hautefeuille, Compt. rend. 73, 563) is of doubtful existence.

Hydrofluosilicic acid *v.* Fluorine.

Silico-fluoroform, *trifluorsilicomethane*, $SiHF_3$ is prepared by heating silico-chloroform in sealed copper or glass tubes with an equimolecular quantity of tin fluoride or titanium fluoride for 18 hours at 100°–120°

$$3SnF_4+4SiHCl_3=4SiHF_3+3SnCl_4.$$

Arsenic and antimony fluorides only yield the tetra-fluoride—

$$3SiHCl_3+4SbF_3=3SiF_4+2Sb+2SbCl_3+3HCl$$

while silver and lead fluorides do not react.

It is a colourless, fuming gas, b.p. −80·2°, m.p. −110°. It slowly decomposes in a sealed tube at the ordinary temperature

$$4SiHF_3=2H_2+Si+3SiF_4$$

It burns with a pale blue flame in air, and decomposes water—

$$2SiHF_3+4H_2O=Si(OH)_4+H_2SiF_6+2H_2.$$

With absolute ethyl alcohol it forms ethyl orthosilicate, and with ether, ethyl silico-orthoformate. It dissolves in its own volume of toluene (Ruff and Albert, Ber. 1905, 38, 53).

Silicon and Chlorine.

Silicon tetrachloride $SiCl_4$ is formed—

1. By heating silicon in chlorine gas (Berzelius, 1824).

2. By passing chlorine over a mixture of finely powdered silica and charcoal made into balls with oil, and strongly heated in a porcelain tube.

3. By the action of chlorine upon magnesium

silicide (Gattermann and Weinlig, Ber. 27, 1943), iron silicide (Warren, Chem. News, 66, 113) and other metallic silicides.

Vigouroux (Compt. rend. 1899, 129, 334) obtains it by the action of chlorine at a red heat upon silicon obtained by reducing two parts of silica with one of aluminium, and afterwards treating with (1) hydrochloric acid, (2) aqua regia.

It is a colourless liquid, b.p. 56·9°, m.p. −89°, sp.gr. 1·524. (For other physical properties, *v.* Thorpe, Chem. Soc. Trans. 1880, 237.)

It is decomposed by water, giving silicic and hydrochloric acids, and by potassium when heated in the vapour, silicon being formed.

If repeatedly passed over silicon heated in a porcelain tube to nearly the softening point of porcelain, with exclusion of air, 'sub-chlorides' were found to be formed by Troost and Hautefeuille (Compt. rend. 73, 563) which could be separated by fractional distillation.

It reacts with ammonia in benzene solution, the product usually isolated being $SiCl_4{\cdot}6NH_3$ (v. *Silicon and Nitrogen*).

Phosphine is not absorbed at ordinary temperatures, but at −23°, 20 volumes are absorbed, which are given off unchanged at 20°. At −80°, 40 vols. (corresponding to $SiCl_4{\cdot}2PH_3$), small, highly refractive crystals are formed at 16° under 20 atmospheres pressure, disappearing at 15 atm. but reforming when the temperature falls to 0°. They are formed at −35° under ordinary pressure. Their composition is not known (Besson, Compt. rend. 110, 240).

The rate of hydrolysis of silicon chloride is greater than that of the corresponding tin and titanium compounds (*v.* Kowalewsky, Zeitsch. anorg. Chem. 1900, 25, 189).

Heated with the equivalent quantity of carbon tetrabromide, silicon bromide is formed in 12 p.c. yield (Gustavson, Ann. Chim. Phys. [5] 2, 200). With organic compounds a number of organic derivatives have been obtained (*q.v.*).

Silicon hexachloride, *hexachlorsilico-ethane*, Si_2Cl_6 is obtained along with the tetrachloride from the action of chlorine upon magnesium silicide, and may be separated by fractional distillation (Gattermann and Weinlig, Ber. 27, 1943). Also by gently heating a mixture of silicon hexaiodide with mercuric chloride, rectifying and purifying by fractional distillation (Friedel, Compt. rend. 73, 1011).

Besson and Fournier (*ibid.* 1909, 148, 839) have obtained it along with other chlorides by submitting silico-chloroform, or silicon tetrachloride mixed with hydrogen to the action of the silent electric discharge.

It is a colourless mobile liquid, fuming in moist air; b.p. 145°–146°. It crystallises in leaflets at −1°. Its vapour density (Friedel and Ladenburg, Ann. Chim. Phys. [5] 19, 390) at 239·4 is 9·7 (air=1). Calculated, 9·29; sp.gr. 1·58. Dilute ammonia gives hydrogen and silicic acid. Strongly heated it gives off an inflammable vapour, and is completely decomposed on heating to 800° in closed vessels.

With ammonia in benzene solution, the compound $Si_2Cl_6{\cdot}10NH_3$ is produced, stable up to 100°, but with phosphine reduction takes place even at −10° (Besson, Compt. rend. 110, 516).

With chlorobenzene and sodium, instead of the hexaphenyl derivative, the tetraphenyl derivative is produced, m.p. 231°, which is also the case with silico-chloroform, indicating the great tendency of silicon to form tetra- derivatives (Gattermann and Weinlig, Ber. 27, 1943). With water, *silico-oxalic acid* (*q.v.*) is produced.

Silicon dichloride Si_2Cl_4 (?) is said to be formed with other products when silicon tetrachloride is passed over heated silicon (Troost and Hautefeuille, Compt. rend. 73, 563). It has not since been investigated.

Silicon octochloride, *octachloro-silicopropane*, Si_3Cl_8 has also been separated from the crude silicon tetrachloride obtained from the action of chlorine upon impure silicon prepared from silica with excess of magnesium. If the silicide formed is previously removed with hydrochloric acid, very little octochloride is formed. Exposed to air, *silico-mesoxalic acid* is produced (Gattermann and Ellery, Ber. 1899, 32, 1114). It is also amongst the products obtained in the action of the silent electric discharge on silico chloroform. Its m.p. is −67°, and its b.p. 215°–218° (Besson and Fournier, Compt. rend. 148, 839).

Decachlorosilico-butane Si_4Cl_{10}, b.p. 149°–151°/15 mm.

Dodecachlorosilico-pentane Si_5Cl_{12}, b.p. 190°/15 mm.

Tetradecachloro-silico hexane Si_6Cl_{14}, m.p. 170° (decomp. but sublimes *in vacuô* at 200°), and a glassy reddish-yellow residue, stable at 200° and soluble in carbon tetrachloride, probably a mixture of solid chlorides, have also been obtained (Besson and Fournier, *l.c.*; *ibid.* 149, 34).

Silico-chloroform, *trichlorosilico-methane*, $SiHCl_3$ is prepared by the action of dry hydrogen chloride upon:—

1. Silicon at red heat (Wöhler and Buff, Annalen, 104, 94; Friedel and Ladenburg, *ibid.* 143, 119);
2. Magnesium silicide at 450°–500° (Gattermann and Weinlig, Ber. 27, 1943);
3. Iron silicide (Warren, Chem. News, 66, 113);
4. Copper silicide (Combes, Compt. rend. 122, 531; Ruff, Albert and Geisel, Ber. 1905, 38, 2222).

The product is condensed by liquid air and freed from silicon tetrachloride by fractional distillation. Where liquid air is not available considerable loss is prevented by absorbing in toluene. It is a colourless liquid, b.p. 33°; m.p. −134° sp.gr. 1·3438 at 15°, which fumes strongly in moist air and gives an inflammable vapour. It is completely miscible with CS_2, CCl_4, $CHCl_3$, $SnCl_4$, $TiCl_4$, $AsCl_3$. It decomposes at 800°, the action being reversible—

$$4SiHCl_3 \rightleftarrows Si+3SiCl_4+2H_2.$$

It is not attacked at 150° by sodium or other metals.

It reacts with dry oxygen, ozone, sulphuric anhydride, and chromic anhydride, giving oxychlorides. Nitric peroxide at −20° reacts explosively, but in carbon tetrachloride solution the following reaction takes place—

$$SiHCl_3+2NO_2=SiO_2+2NOCl+HCl$$

(Besson and Fournier, Compt. rend. 1909, 148, 1192).

With excess of aniline in benzene solution *trianilino siliconhydride* $SiH(NHPh)_3$ is formed (from which $SiHCl_3$ is regenerated by dry hydrogen chloride) in slender white needles, which begin to decompose at 114°. With ammonia *silicon nitrogen hydride* (*q.v.*) is produced.

With absolute ethyl alcohol it yields *triethyl silico-orthoformate*, b.p. 134°–137° (Friedel and Ladenburg, Ann. Chim. Phys. 1871 [4] 23, 430), and with water *silico-formic anhydride*, a white powder resembling silica, stable at 150°, which burns in air, and evolves hydrogen with potassium hydroxide

$$(SiOH)_2O+8KOH=2Si(OK)_4+3H_2+3H_2O.$$

It is decomposed by chlorine at ordinary temperatures, giving silicon tetrachloride and hydrogen chloride.

Monochlorosilico-methane SiH_3Cl and *dichlorosilico-methane* SiH_2Cl_2 are obtained by fractionating the difficultly condensible products formed in the action of dry hydrogen chloride upon amorphous silicon. Their b.ps. are about −10° and +12° respectively. They are colourless, mobile, highly expansive liquids, which yield hydrogen with water and alkalis.

Silico-hydric chloride, obtained by Wöhler and Buff by passing hydrogen chloride over silicon at low redness, and to which they assigned the formula $Si_3H_4Cl_{10}$ (Annalen, 104, 94), has been shown by Friedel and Ladenburg (Bull. Soc. chim. [2] 7, 322) to be a mixture of silicon tetrachloride and silico-chloroform.

SILICON OXYCHLORIDES.

Considerable interest attaches to these compounds in regard to the constitution of the silicic acids.

Trichlorosilicic oxide $(SiCl_3)_2O$ is obtained by passing the vapour of silicon tetrachloride through an exhausted porcelain tube containing fragments of felspar, heated to near the softening point of felspar. On re-passing the vapour several times, and fractionating the product, the oxychloride passes over between 136° and 139°.

It is also formed, together with phosphorus oxychloride, when silicon tetrachloride is passed over strongly heated phosphoric anhydride.

It is a colourless, fuming liquid, of v.d. 10·05 (air=1). It is decomposed by water and alcohol, forming with the latter *disilicohexylic ether* $[Si(OC_2H_5)_3]_2O$, b.p. 235°–237°.

Heated with three molecular proportions of zinc ethyl, *triethyl silicic oxide* $[Si(C_2H_5)_3]_2O$ is produced (Friedel and Ladenburg, Bull. Soc. chim. [2] 9, 358).

It is also formed from silico-chloroform by the action of dry oxygen or ozone (Besson and Fournier, Compt. rend. 1909, 148, 1192), and when chlorine, mixed with half its volume of oxygen, is passed over heated silicon (Troost and Hautefeuille, Bull. Soc. chim. [2] 35, 360).

Several oxychlorides are produced by the action of the induction spark on a mixture of the tetrachloride, trichlorosilicic oxide, and oxygen, or by passing trichlorosilicic oxide, together with oxygen, several times over fragments of porcelain heated in a glass tube, the compounds having the molecular formulæ $Si_4O_3Cl_{10}$ and $Si_4O_4Cl_8$, boiling at 153° and 200° respectively, being obtained in largest quantity.

The following have been separated by fractional distillation :—

	Formula	Boiling-point
1.	Si_2OCl_6	136°–139°
2.	Si_4OCl_{14}	—
3.	$Si_4O_3Cl_{10}$	152°–154°
4.	$Si_4O_4Cl_8$	198°–202°
5.	$Si_4O_6Cl_4$	about 400°
6.	$Si_4O_7Cl_2$	about 440°
7.	$Si_8O_{10}Cl_{12}$	—

(Troost and Hautefeuille, Compt. rend. 73, 563; the formulæ have been adjusted to the new atomic weights).

The constitution of (1) is undoubtedly

$$Cl_3{\equiv}Si{-}O{-}Si{\equiv}Cl_3 \text{ or } Si_2OCl_6.$$

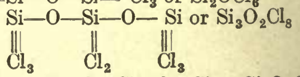
By successive replacement of chlorine by oxygen the following formulæ are derived—

$$Cl_2{=}Si{=}O_2{=}Si{=}Cl_2 \text{ or } Si_2O_2Cl_4$$
$$Cl{-}Si{\equiv}O_3{\equiv}Si{-}Cl \text{ or } Si_2O_3Cl_2$$
$$Si{\equiv}O_4{\equiv}Si \text{ or } Si_2O_4, \text{ or } SiO_2.$$

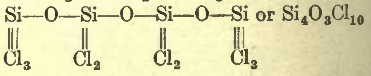
These correspond to the oxychlorides 4 and 5 respectively.

Further, by substitution of the radicle —O—$SiCl_3$ for chlorine, the following formulæ may be derived from $SiCl_4$—

$$Cl_3{\equiv}Si{-}O{-}Si{\equiv}Cl_3 \text{ or } Si_2OCl_6$$



$$\begin{array}{ccccc} Si & -O- & Si & -O- & Si \\ ||| & & || & & ||| \\ Cl_3 & & Cl_2 & & Cl_3 \end{array} \text{ or } Si_3O_2Cl_8$$



$$\begin{array}{ccccccc} Si & -O- & Si & -O- & Si & -O- & Si \\ ||| & & || & & || & & ||| \\ Cl_3 & & Cl_2 & & Cl_2 & & Cl_3 \end{array} \text{ or } Si_4O_3Cl_{10}$$

The last corresponds to 3, and by successively replacing pairs of chlorine atoms by oxygen the formulæ $Si_4O_4Cl_8$, $Si_4O_5Cl_6$, $Si_4O_6Cl_4$, and $Si_4O_7Cl_2$, corresponding to 4, 7, 5, and 6 respectively may be derived.

Formula 2 would appear to be inadmissible.

The above structural formulæ may be written generally—

$$Cl_3Si{-}(O{-}Si(Cl_2){-})_n{-}O{-}SiCl_3,$$

or $$Si_{n+2}O_{n+1}Cl_{2n+6}$$

and the corresponding silicic acids

$$(OH)_3Si{-}(O{-}Si(OH)_2{-})_n{-}O{-}Si(OH)_3,$$

or $$Si_{n+2}O_{\ +1}(OH)_{2n+6}.$$

SILICON AND BROMINE.

Silicon tetrabromide $SiBr_4$ is produced by passing bromine vapour (1) over an intimate mixture of silica and charcoal (Serullas), (2) over heated silicon, or magnesium silicide (Gattermann, Ber. 22, 186), and (3) in large yield along with silicobromoform, using hydrogen bromide instead of bromine in (2) (Gattermann, *l.c.*).

(4) By heating silicon tetrachloride with carbon tetrabromide (Gustavson, Ann. Chim. Phys. [5] 2, 200).

A colourless, fuming liquid, m.p. +5°, b.p. 150·8°/751·4 mm. (Blix), sp.gr. 2·82 (Reynolds) with very regular thermal expansion.

In general properties it resembles the chloride, but differs from it in its vigorous and sometimes explosive reaction with potassium on very slight warming, and in undergoing no reduction when mixed with hydrogen and submitted to the action of the silent electric discharge. It combines with ammonia very slowly, yielding $SiBr_4{\cdot}7NH_3$. Phosphine under ordinary pressure does not combine even at solidifying temperature, but on prolonged compression a colourless liquid is formed which changes to a white amorphous solid (Besson, Compt. rend. 110, 240).

Like the chloride, it readily forms organic derivatives.

Monobromo-silico-methane SiH_3Br, b.p. 30°–40°, and *dibromo-silico-methane* SiH_2Br_2, b.p. 75°, are spontaneously inflammable liquids obtained in small quantity by fractional distillation of the crude tetrabromide (Besson and Fournier, Compt. rend. 1910, 151, 1055).

Silico - bromoform, *tribromsilico - methane* $SiHBr_3$ is also obtained thus, but is more easily obtained by the action of dry hydrogen bromide on—

1. Magnesium silicide, although only in small yield, as is the case with silicon and hydrogen bromide, the chief product being the tetrabromide (Gattermann, Ber. 22, 186).
2. Copper silicide (Combes, Compt. rend. 1896, 122, 531).
3. Trianilino silico methane (Ruff, Ber. 1908, 41, 3738).

A colourless, fuming liquid, b.p. 109°–111°, remains liquid at −60° (Besson), sp.gr. 2·7. It is analogous in chemical properties to silicochloroform, but is less stable than the latter.

Silicon hexabromide, *hexabromosilico-ethane* Si_2Br_6, is prepared by adding an equivalent of bromine to a solution of the hexaiodide in carbon disulphide, it crystallises in rhombic plates, which are isomorphous with the corresponding iodide (Friedel and Ladenburg, Ann. Chim. Phys. [5] 19, 390). It is also obtained when silicobromoform is submitted to the action of the silent electric discharge (Besson and Fournier, *l.c.*).

It melts at 95° and boils at 265°.

Octrabromosilico-pentane Si_3Br_8, m.p. 133°, and *decabromosilico-butane* Si_4Br_{10}, m.p. 185° (decomp.) have also been obtained by this method.

Disilicohydric pentabromide Si_2HBr_5, m.p. 89°, b.p. 230° (Mahn, Jahresber. 1869, 248), is probably impure Si_2Br_6.

Trisilicohydric bromide $Si_3H_4Br_{10}$ (Wöhler and Buff, Annalen, 104, 94) is a mixture of $SiBr_4$ and $SiHBr_3$.

Silicon and Iodine.

Silicon tetriodide SiI_4 is obtained by passing iodine vapour in a stream of carbon dioxide, through a long porcelain tube filled with silicon and heated to redness. The product sublimes in the cool part of the tube as a white crystalline mass. It is purified by dissolving in carbon disulphide and agitating with mercury.

It crystallises by sublimation or from its solution in carbon disulphide in colourless transparent regular octahedra; melts at 120·5° to a yellow liquid; boils about 290°, and distils unaltered in a stream of carbon dioxide. Vapour density=19·12 at 360°. The vapour burns with a red flame, depositing iodine. It is decomposed by water and alcohol

$$SiI_4+2C_2H_6O=SiO_2+2C_2H_5I+2HI$$

and by ether at 100°, yielding silicic ether

$$SiI_4+4(C_2H_5)_2O=4C_2H_5I+Si(OC_2H_5)_4$$

(Friedel, Annalen, 149, 96).

It has also been prepared by passing iodine vapour with carbon dioxide over the magnesium-silica reduction product at red heat (Gattermann, Ber. 22, 190a).

Silicon hexaiodide Si_2I_6. When the tetriodide is heated to 300° with finely divided silver, a white mass is obtained, which is purified by repeated treatment with small quantities of carbon disulphide and ultimate solution with the aid of heat in that solvent. On cooling, the hexaiodide separates out in colourless hexagonal prisms, which fume on exposure to air. It is decomposed by potash, forming silica, hydriodic acid, and free hydrogen.

It may be fused *in vacuô* at 250°, undergoing partial decomposition (Friedel and Ladenburg, Ann. Chim. Phys. [5] 19, 390).

Gently warmed with zinc ethyl it yields on distillation a mixture of silicon tetraethyl, b.p. 150°–154°, and silicon triethyl, b.p. 250°–253°, which may be separated by fractionation (Friedel and Ladenburg, Compt. rend. 68, 920).

Silicon di-iodide Si_2I_4 is described by Friedel and Ladenburg (*ibid.* 68, 920; Bull. Soc. chim. [2] 12, 92) as an orange-red substance, insoluble in CS_2, $CHCl_3$, and $SiCl_4$, decomposed by water and evolving hydrogen with potassium hydroxide, produced by the dry distillation of Si_2I_6.

Silico-iodoform $SiHI_3$ was prepared by Friedel and Ladenburg (*l.c.*) by passing hydrogen iodide mixed with hydrogen over crystalline silicon and fractionating the product.

It is obtained in fair yield by the action of dry hydrogen iodide on silico nitrogen hydride suspended in cold carbon disulphide, and, in still better yield, from its action on trianilino silico-methane in benzene (Ruff, Ber. 1908, 41, 3738).

A colourless, strongly refracting liquid, sp.gr. 3·362 at 0°, 3·314 at 20°. It boils at 220°, but decomposes slowly above 150°, and if kept boiling the temperature gradually rises to 300°, the residue being the tetraiodide. It can, however, be distilled under reduced pressure. It is decomposed by water in a manner similar to silico-chloroform.

Hydrosilicic iodide is the name given by Wöhler and Buff to the substance obtained by passing hydriodic acid over heated crystalline silicon (Annalen, 104, 99). This has been shown by Friedel and Ladenburg (*l.c.*) to be a mixture of silicic iodide, free iodine, and silico-iodoform $SiHI_3$.

Mixed Halogen Derivatives.

Silicon chlorobromides. A *trichlorobromide* $SiCl_3Br$ is obtained by the action of bromine upon silicic chloroform. It is a colourless, fuming liquid, boiling at 80°, and decomposed by water. A *dichlorobromide* $SiCl_2Br_2$ is also formed in the above reaction, and is found amongst the products boiling at 100° (Friedel and Ladenburg, Ann. Chim. Phys. [4] 27, 416).

The *trichlorobromide* is also obtained without the second product by the action of Br upon the trichlorosulphydrate (*q.v.*) (Friedel and Ladenburg, *l.c.*).

$SiClBr_3$ was obtained by Reynolds from the tetrabromide (Chem. Soc. Trans. 1887, 590).

They may also be obtained by passing a mixture of hydrogen bromide and silicon chloride through a red-hot tube, shaking the condensed product with mercury and fractionating (Besson, Compt. rend. 112, 788).

Silicon chloroiodides. The three chloroiodides are present in the product obtained by passing iodine chloride vapour over crystalline silicon at nearly red heat (Besson, *ibid.* 112, 1314). They are also formed when hydrogen iodide and silicon chloride vapour are passed through glass tubes heated to redness.

The *trichloroiodide* is also formed by heating silicon chloride and iodine in sealed tubes at 200°–250°, and the *dichloroiodide* by saturating the trichloroiodide with hydrogen chloride at −22°, and heating in sealed tubes at 250°.

They are colourless, fuming liquids, liberating iodine on exposure to light, and burn with liberation of iodine (Besson, *ibid.* 611). Silicon bromoiodides are obtained by distilling iodine bromide over crystalline silicon at nearly red heat, and fractionating the product over copper.

The *tribromoiodide* results on heating silicobromoform with iodine in sealed tubes at 200°–250°, and from the action of hydrogen iodide on silicon bromide at red heat (Besson, *ibid.* 1447).

The mixed halogen compounds, like the simple ones, give definite compounds with ammonia.

The melting- and boiling-points of the above compounds, as determined by Besson, are tabulated below—

Formula	M.p.	B.p.
$SiCl_3Br$	—	80°
$SiCl_2Br_2$	—	103°–105°
$SiClBr_3$	−39°	126°–128°
$SiCl_3I$	—	113°–114°
$SiCl_2I_2$	—	172°
$SiClI_3$	2°	234°–237°
$SiBr_3I$	14°	192°
$SiBr_2I_2$	38°	230°–231°
$SiBrI_3$	53°	255°

SILICON AND NITROGEN.

Silicon nitrides. Deville and Wöhler obtained by the action of ammonia on silicon chloride, and by strongly heating crystalline silicon in nitrogen or air, a white amorphous infusible mass, indifferent to most reagents, although slowly evolving ammonia in moist air, which they concluded to be silicon nitride without, however, ascertaining its composition (Annalen, 104, 256; 110, 248).

By heating crystalline silicon with gas carbon in a blast furnace Schützenberger (Compt. rend. 89, 644) obtained a mixture of silica with a green and a white substance, to which he assigned the formulæ $(SiN)_x$ and Si_3N_4 respectively, the former being insoluble in hydrofluoric acid, the latter soluble.

By heating crystalline silicon in pure nitrogen, and treating the white mass so produced with potassium hydroxide, and then with hydrofluoric acid, a residue is obtained having the composition Si_2N_3 (Schützenberger and Colson, Compt. rend. 93, 1508).

According to Weiss and Engelhardt (Zeitsch. anorg. Chem. 1909, 65, 38) silicon begins to combine with nitrogen at about 1240°, the rate of combination increasing rapidly with rise of temperature. The bulky amorphous product consists of nitrides mixed with silicon.

Silicon mononitride SiN is the residue remaining when the product is boiled with a mixture of nitric and hydrofluoric acids and then ignited and washed with hydrochloric acid. It is white and of sp.gr. 3·17.

Silicon sesquinitride Si_2N_3 is obtained if the crude product is boiled first with potassium hydroxide, and then with hydrofluoric acid. It still contains silica which cannot be removed. Its sp.gr. is 3·64.

Trisilico-tetranitride Si_3N_4, sp.gr. 3·44, is formed when silicon is heated in nitrogen at 1300°–1400°, until saturated, and is only slightly decomposed by treatment with potassium hydroxide, hydrofluoric acid, or a mixture of hydrofluoric and nitric acids. The other nitrides are readily attacked. The sesquinitride is converted by the latter mixture into the mononitride (*v.* also *Siliconimide*).

By heating silicon in the flame of a coke fire a substance having approximately the formula Si_3C_3N is formed (*l.c.*).

Siliconamide $Si(NH_2)_4$ is the first product obtained in the reaction between benzene solutions of silicon chloride and ammonia (Lengfield, Amer. Chem. J. 1899, 21, 531; *v.* also Ruff, Ber. 1908, 41, 3744). It is a white solid, easily losing ammonia and yielding

Siliconimide $(SiNH)_2$. The product usually isolated is $SiCl_4{\cdot}6NH_3$, which, as it loses one-third of its ammonia when thrown into water, may be looked upon as $Si(NH)_2{\cdot}4NH_4Cl$ (Lengfield, *l.c.*; *v.* also Gattermann, Ber. 22, 186). It is probably identical with

Silico-cyanamide $SiN{\cdot}NH_2$, described by Harris (Chem. Zentr. 1889, ii. 283) as obtained from the action of dry ammonia upon silicon chloride.

According to Blix (Ber. 1903, 36, 4220) $Si(NH)_2$ is also obtained by the action of liquid ammonia on silicon thiochloride. When heated to 900° it loses ammonia and leaves

Silicon nitrimide Si_2N_3H (*cf.* Schützenberger and Colson, Compt. rend. 92, 1508), which further loses ammonia at 1200°–1300°, leaving Si_3N_4.

Silico-nitrogen hydride $SiH\vdots N$ is the product obtained by washing with liquid ammonia the powder obtained from the action of dry ammonia diluted with hydrogen, on silico-chloroform at −10°. With water or potassium hydroxide the following quantitative reaction takes place—

$$SiH\vdots N+4KOH=Si(OK)_4+NH_3+H_2.$$

it possesses the reducing properties of silico formic anhydride, and is converted by dry hydrogen chloride at 300° into silico-chloroform and ammonium chloride (Ruff, Albert and Geisel, Ber. 1905, 38, 53).

The substance $Si_5N_6Cl_2$ is formed as a white powder when the product of the reaction of dry ammonia upon silicon chloride is heated to redness in a current of hydrogen. On heating this to redness in a current of ammonia it loses chlorine, and is converted into Si_2N_3H (Schützenberger and Colson, Compt. rend. 92, 1508).

SILICON AND CARBON.

Silicon carbide *v.* CARBORUNDUM.

Silicon dicarbide SiC_2 is formed by passing ethylene, or hydrogen saturated with benzene, over silicon heated to whiteness in a porcelain tube. It is not attacked by acids, nor by oxygen or chlorine at red heat, but is decomposed by fused potassium hydroxide, or a mixture of lead oxide and chromate (Colson, Compt. rend. 94, 1316, 1526).

Oxycarbides of the formulæ $SiCO$, $SiCO_2$, $SiCO_3$, Si_2C_2O, Si_2C_3O, $Si_2C_3O_2$, and $Si_2C_4O_4$ have been prepared (Colson and Schützenberger, *ibid.* 93, 1508; Colson, *ibid.* 94, 1316, 1526).

Siloxicon. The commercial name for the product obtained by Acheson in 1899 by electrically heating together graphite and silica. Is a mixture of silicon carbide and oxycarbides. It is highly refractory, and eminently suitable for resistant crucibles, firebricks, furnace linings, &c., but is not now used to any extent (J. Soc. Chem. Ind. 1910, 245).

A sample gave on analysis—

Si_2C_2O, 71·39 p.c.; $SiCO_3$, 10·81 p.c.; SiC 5·81 p.c.; graphite, 10·06 p.c.; Fe, 1·07 p.c.; impurities, 0·86 p.c. (Spielmann, *ibid.* 1905, 24, 654).

The *substances* Si_4C_4S and Si_2C_2N have also been described (Colson, Compt. rend. 94, 1316, 1526; Schützenberger and Colson, *ibid.* 92, 1508).

Silicon thiocyanate was obtained by Miguel (Ann. Chim. Phys. 1877, [v.] ii. 343) by heating lead thiocyanate with silicon tetrachloride to about 350°. Reynolds (Chem. Soc. Trans. 1906, 397) obtains a better yield by heating 100 grms. of the dehydrated and powdered salt with 17 grms. of silicon chloride in 400 c.c. of benzene on the water-bath with reflux condenser. The hot liquid is filtered and after distilling off a portion of the benzene, crystallised, m.p. 143·8°, b.p. 314·2°. Stable at red heat, v.d. 259° ($Si(SCN)_4$ 260). Its stability shows it to be $Si(SCN)_4$ rather than $Si(NCS)_4$.

SILICON AND PHOSPHORUS.

Silicon phosphide is formed according to Gewecke (Annalen, 1908, 361, 89) by the action of phosphine upon silicon chloride. *See*, however, Besson under *Silicon chloride.*

Silicon phosphate. When precipitated silica is dissolved in fused metaphosphoric acid, and the mass extracted with water, transparent, colourless octahedra are obtained, sp.gr. 3·1, which scratch glass, and melt on platinum under the blow-pipe to a glass which does not devitrify on cooling; formula $SiO_2{\cdot}P_2O_5$. It exists also as hexagonal crystals and monoclinic prisms, and also in the hydrated form $SiO_2P_2O_5,4H_2O$ (Hautefeuille and Margottet, Compt. rend. 96, 1052; 99, 780; 104, 56).

SILICON AND BORON.

Silicon triboride and **silicon hexaboride** are produced by heating 1 part of boron with 5 parts of silicon electrically in a clay crucible for about a minute. The residue after treating with a mixture of nitric and hydrofluoric acids, then with hot potassium hydroxide, and finally with dilute nitric acid, yields the two borides SiB_3 and SiB_6 with 80–90 p.c. of the latter.

The hexaboride is readily oxidised by boiling nitric acid, while the triboride is very slowly attacked, but the latter is decomposed by fused potassium hydroxide, which leaves the former unchanged. Thus both can be obtained in pure condition.

SiB_3 forms black rhombic plates, sp.gr. 2·52.

SiB_6 forms black opaque irregular crystals, sp.gr. 2·47.

Both are decomposed by fluorine on warming, and by chlorine and bromine at a higher temperature, but not by iodine or nitrogen or by halogen acids. They are superficially oxidised in air, and readily decomposed by potassium carbonate or fusion mixture (Moissan and Stock, Compt. rend. 1900, 131, 139).

SILICON AND SULPHUR.

Silicon disulphide SiS_2 was first prepared by Berzelius, by the union of sulphur and amorphous silicon.

It is produced by passing the vapour of carbon disulphide over a mixture of silica and lampblack made into balls and ignited, and is deposited in the cool parts of the tube in asbestiform needles (Fremy, Ann. Chim. Phys. [3] 38, 314).

When dry hydrogen sulphide is passed over crystallised silicon at a red heat, fine white needles of the disulphide are produced. A yellowish sublimate is formed at the same time, probably consisting of Si_3S_4 (Sabatier, Bull. Soc. chim. [2] 38, 153).

It is formed in the decomposition of silicon thiochloride (Blix, Ber. 1903, 36, 4218).

Fielding (Trans. Faraday Soc. 1909, 5, 110) obtained it in an impure state by heating ferrosilicon with ferrous sulphide in a vacuum.

It is best prepared by heating amorphous silicon with three times the quantity of sulphur at 150°, and afterwards at a red heat. It is purified by subliming in a porcelain tube under reduced pressure (60 mm.) (Hempel and Haasy, Zeitsch. anorg. Chem. 23, 32).

When pure it is obtained in white needle-shaped crystals, which sublime unchanged. It decomposes rapidly in contact with moist air, forming hydrogen sulphide and silica. Alcohol and ether act upon it in the cold. Nitric acid decomposes it, with separation of sulphur, and formation of silicic and sulphuric acids. Hydrogen has no action upon it (Fremy). It combines readily with sodium sulphide (Hempel and Hassy), and with potassium sulphide (Berzelius).

Heat of formation—

Si (amorph.)$+S_2$ (solid)$=SiS_2+40400$ cal.

Heat of decomposition—

SiS_2+H_2O evolves 38800 cal. (Sabatier, Compt. rend. 90, 819).

Silicon monosulphide SiS is obtained as a yellow sublimate, together with another yellowish substance, an oxysulphide $SiSO$, on passing carbon disulphide vapour over silicon at a white heat.

If the contents of the tube are treated with potash and hydrofluoric acid, a greenish powder is obtained having the composition Si_4C_4S, which is converted into $Si_4C_4O_2$ by heating in a current of oxygen (A. Colson, Bull. Soc. chim. [2] 38, 56; Compt. rend. 94, 1526).

In addition to SiSO another oxysulphide $SiSO_2$ has been investigated (Rankin and Revington, Chem. Soc. Proc. 1908, 131).

Cambi (Atti. R. Accad. Lincei, 1910, [v.] 19, ii. 294) by heating ferrosilicon and sulphur in an electric furnace, and subliming the grey mass so formed, obtained the monosulphide in two forms, as a black vitreous solid, and as a yellow powder. Either form gives both on sublimation. The black variety is of sp.gr. 1·853. Both forms are decomposed by alkalis as follows: $SiS+2KOH=SiO_2+K_2S+H_2$; and with water they evolve hydrogen sulphide and leave residues of uncertain composition.

A **silico-hydric sulphide** $Si_4H_8S_5$, corresponding to the oxygen compound, is formed by the action of aqueous sulphurous acid mixed with a little hydrochloric acid upon calcium silicide (Wöhler, Annalen, 127, 257).

A *sulphochloride* of silicon was obtained by Pierre, who gave it the formula $Si_3S_4Cl_8$, by passing a mixture of silicon chloride vapour and dry sulphuretted hydrogen gas through a red-hot porcelain tube, distilling the product, and collecting what passed over at 90°–100° (Pierre, Annalen, 69, 73).

Friedel and Ladenburg assign to it the name *silicon chlorosulphydrate* and the formula $SiCl_3SH$ or *silico- mercaptan.* It is a colourless liquid, boiling at 96°, decomposing on exposure to the air into hydrochloric and sulphydric acids and silica. With alcohol, in the proportion of 3 mols. alcohol and 1 mol. of the body, it forms $SiSH(OC_2H_5)_3$, but an excess of alcohol converts it into silicic ether $Si(C_2H_5O)_4$.

With bromine it forms a trichlorobromide (Friedel and Ladenburg, Ann. Chim. Phys. [4] 27, 416; *v.* also Bull. Soc. chim. [2] 7, 472).

At higher temperatures the action of silicon chloride on hydrogen sulphide gives **silicon thiochloride** $SiSCl_2$, which, crystallised from chloroform, melts at 75° and boils at 92°/22·5 mm. It decomposes on boiling into SiS_2 and $SiCl_4$, and with liquid ammonia gives $Si(NH)_2$ (Blix, Ber. 1903, 36, 4218).

It is also formed along with SiS_2 by passing chlorine and sulphur chloride vapour over crystalline silicon at bright-red heat. It can be sublimed in a current of dry air at 100° (Besson, Compt. rend. 113, 1040).

Silicon thiobromide $SiSBr_2$ is obtained from silicon bromide and hydrogen sulphide at 150° in presence of aluminium bromide, m.p. 93°, b.p. 150°/18·3 mm. Dry ammonia in benzene solution yields *silicon thiourea* $SiS(NH_2)_2$ (Blix, *l.c.*).

Silicon selenide $SiSe_2$ is produced by passing dry hydrogen selenide over crystalline silicon at a red heat, as a semi-metallic lustrous hard mass with an irritating odour. It is decomposed by cold water, more readily by potash, evolving hydrogen selenide. It is converted by oxygen at a red heat into silica, selenious anhydride and selenium (Sabatier, Compt, rend. 113, 132).

Wöhler (Annalen, 127, 257) describes compounds of selenium and tellurium analogous to the silico-hydric sulphide described above.

METALLIC SILICIDES.

Magnesium, calcium, strontium, and barium reduce the oxide with formation of silicides. Crystalline silicides have been prepared from iron, chromium, nickel, cobalt, manganese, copper, platinum, and other metals, usually by direct union of the elements, or by heating the metal in silicon chloride vapour.

Potassium, sodium, aluminium, zinc, lead, tin, bismuth, antimony, gold, and silver dissolve it when in the molten state, but re-deposit it on cooling, without forming compounds.

Lithium silicide Li_6Si_2 is remarkable in that with concentrated hydrochloric acid *silicohexane* Si_2H_6 is evolved. Dilute acid gives hydrogen. Heated in dry hydrogen chloride, lithium and silicon chlorides are formed and hydrogen liberated (Moissan, Compt. rend. 1902, 135, 1284).

Calcium silicide $CaSi_2$ was obtained by Wöhler by heating together graphitoidal silicon (300 grms.), calcium chloride (3000 grms.), and sodium (350) grms. covered with another 350 grms. of sodium, and, lastly, with a layer of common salt, in a covered crucible, to bright-red heat (Annalen, 126, 257). It is thus obtained as a button with metallic lustre, lead grey colour, and scaly crystalline structure, crumbling on exposure to air.

It is also formed by heating silicon and lime in an ordinary furnace with calcium fluoride or chloride as flux (Goldschmidt, D. R. P. 199193), or with carbon in the electric furnace (de Chalmot, Amer. Chem. J. 1896, 18, 536). With water and dilute acids hydrogen is evolved, but little, if any, silicon hydride (*v.* however, Bradley, Chem. News. 82, 149; Chem. Zentr. 1900, ii. 890).

According to Le Chatelier (Bull. Soc. chim. 1897, [iii.] 17, 793) it exists in two varieties, the first scarcely attacked by concentrated nitric acid, and leaving a yellow *silicone* on treatment with hydrochloric acid; the second readily attacked by nitric acid, and giving a white residue with hydrochloric acid. Usually a mixture of these residues is obtained, the composition of which varies from $Si_2O_4H_4$ to $Si_2O_3H_4$.

Tricalcium disilicide Ca_3Si_2 is described by Hackspill (*ibid.* 1908, [iv.] 3, 619) as being obtained by compressing a mixture of calcium filings and powdered silicon into a calcium cylinder enclosed in one of iron, and heated to 1000° in a porcelain tube. Excess of calcium is removed by sugar solution, and the slender needles of the silicide washed with alcohol and ether, sp.gr. 1·64. This silicide is attacked by halogens in the cold, and by oxygen at red heat. Dilute acids give spontaneously inflammable hydride, as with lithium silicide (*v.* also Hönigschmid, Monatsh. 1909, 30, 497).

Several alloys have been prepared by Tamaru (Zeitsch. anorg. Chem. 1909, 62, 81).

Strontium silicide $SrSi_2$ is prepared like the corresponding calcium compound, but according to Bradley (*l.c.*) differs from the latter in that no silico-acetylene is evolved with acids.

Barium silicide $BaSi_2$. Barium peroxide and silicon react violently when the action is initiated by means of a fuse. With 50 parts BaO_2 and 15 parts Si, a barium silicide containing 30 p.c. Ba is obtained (Askenasy and Ponnaz, Zeitsch. Elektrochem. 1908, 14, 810).

Barium chloride (and also other difficultly volatile chlorides, as those of calcium and manganese) give the silicide when heated with silicon in the electric furnace (Jüngst and Mewes, D. R. P. 15716). They yield hydrogen silicide with dilute or concentrated hydrochloric acid.

Magnesium silicide. According to Wöhler (*l.c.*) when magnesium chloride, sodium chloride, sodium silicofluoride, and metallic sodium are fused together for the preparation of silicon hydride, the mass contains, besides free silicon, two magnesium silicides, one of which yields silicon hydride with aqueous ammonium chloride or hydrochloric acid, whilst the other yields hydrogen and silica.

Lebeau and Bossnet (Rev. Metallurgie, 1909, 6, 272), however, as a result of microscopic examination of the various products obtained by heating magnesium, alone and with silicon under potassium silicofluoride, state that only one silicide Mg_2Si exists (*v.* further Winckler, Ber. 23, 2642). It is of slate-blue colour, sp.gr. 2, decomposes cold water slowly with liberation of hydrogen, and with dilute hydrochloric acid yields a mixture of hydrogen and silicon hydrides.

It is also prepared (Moissan and Smiles, Ann. Chim. Phys. 1902, 7, 5) by heating to redness a mixture of silicon and magnesium powder in a porcelain tube in a current of hydrogen, but is most conveniently obtained in a crude form by heating a mixture of sand and magnesium powder in the requisite proportions (v. *Silicon, Preparation of*), m.p. 1102° (Vögel, Zeitsch. anorg. Chem. 1909, 61, 46). Eutectics are formed with 48 p.c. and 4 p.c. of silicon respectively.

Copper silicide. Three products with different silicon content were obtained by Deville and Caron (Annalen, 104, 232; Ann. Chim. Phys. [iii.] 67, 455), but were not definite compounds. Cu_2Si_3 (de Chalmot, Amer. Chem. J. 1896, 18, 95; 1897, 19, 118) and Cu_2Si (Vigouroux, Compt. rend. 1896, 122, 318) have also been described, but according to Lebeau (*ibid.* 142, 154) only

Cuprous silicide Cu_4Si exists, any excess of silicon being uncombined, and in a form insoluble in hydrofluoric acid (*cf.* Moissan and Siemens, *ibid.* 1904, 138, 1299).

The freezing-point curve for Cu and Si shows only one maximum (at 800°) corresponding to Cu_4Si.

It is obtained by fusing together silicon (17 parts) and electrolytic copper (90 parts) in a current of hydrogen, and extracting the uncombined silicon with 5 p.c. sodium carbonate (*v.* also Vigouroux, *ibid.* 1907, 144, 1214; Phillips, Metallurgie, 1907, 4, 587, 613). It is silver-white, turning brick-red on exposure, sp.gr. 7·48 (Vigouroux, Compt. rend. 1906, 142, 87).

Cementation of copper turnings can be effected at 700° with absorption of 9·56 p.c. of silicon.

A dark copper-coloured silicide is said to be formed when copper sulphate is precipitated with silicon hydride. It is readily oxidised, and is decomposed at once by nitric acid. Silicides of silver have been described, but according to Arrivaut (Compt. rend. 1908, 147, 859) are non-existent.

Aluminium and silicon do not combine, though miscible in all proportions in the fused state. The eutectic (10 p.c. Si) melts at 576° (Minet, *ibid.* 112, 1215; Kieser, Chem. Zeit. 1908, 32, 1161; Fraenkel, Zeitsch. anorg. Chem. 1908, 58, 154).

It, however, forms double silicides with a number of other metals (Lévy, Compt. rend. 106, 66; Vigouroux, *ibid.* 141, 951; Manchot and Kieser, Annalen, 1904, 337, 353; Manchot and Fischer, *ibid.* 1907, 357, 129).

Tin, lead, and thallium form no compounds (Tamaru, Zeitsch. anorg. Chem. 1909, 61, 40).

Titanium silicide $TiSi_2$ is produced from the oxide or potassio-fluoride with sand, aluminium, and sulphur, ignited by a Goldschmidt cartridge (U.S. Pat. 923, 152).

Zirconium silicide $ZrSi_2$ is prepared similarly (Hönigschmid, Compt. rend. 1906, 143, 224).

Cerium silicide $CeSi_2$ is obtained together with potassium at the negative pole on electrolysing a fused mixture of potassium fluoride and cerium oxide, and after removal of the potassium with alcohol, remains as a brown powder, insoluble in acids, which burns with a reddish flame (Ulik, Chem. Zentr. 1865, 1045). Prepared by fusing the oxide with silicon in the electric furnace, it differs from the above in being definitely crystalline, and attacked by mineral acids with disengagement of hydrogen (Sterba, Compt. rend. 1902, 135, 170).

Thorium silicide $ThSi_2$ is obtained by heating the double fluoride of potassium and thorium, potassium silicofluoride, and aluminium, at 1200° (Hönigschmid, *ibid.* 1906, 142, 157).

It closely resembles graphite; sp.gr. 7·96.

Vanadium silicides. Two silicides are known, VSi_2 (Moissan and Holt, *ibid.* 1902 135, 78) and V_2Si (*ibid.* 493), produced by heating together vanadium sesquioxide and silicon in the electric furnace. If silicon is in excess the former is obtained, and the latter, produced when excess of V_2O_3 is used, is converted into the former by heating with excess of silicon. VSi_2 is a brilliant metallic crystalline substance, sp.gr. 4·42, harder than glass, and fusible and volatile in the electric furnace. V_2Si, obtained in metallic silvery prismatic crystals, sp.gr. 5·48, is harder and less volatile than VSi_2. Both are somewhat refractory towards most reagents, but are readily attacked by hydrofluoric acid (*v.* further Moissan and Holt, Ann. Chim. Phys. 1902, vii. 27, 277; Gin, Electrochem. and Met. Ind. 1909, 7, 264).

Tantalum silicide $TaSi_2$, *v.* Hönigschmid (Monatsh. 1907. 28, 1017).

Chromium silicides. Cr_2Si is obtained by heating the metal or its oxide with silicon in the electric furnace (Moissan, Compt. rend. 1895, 121, 621).

Cr_3Si_2 is obtained by prolonged heating of silicon chloride with pure chromium at 1200° (Vigouroux, *ibid.* 1907, 144, 83).

Cr_3Si (Zettel, *ibid.* 1898, 126, 833), Cr_2Si, and $CrSi_2$ (de Chalmot, Amer. Chem. J. 1897, 19, 69) are all obtained by fusing copper and the requisite proportions of chromium and silicon together (Lebeau and Figueras, Compt. rend. 1903, 136, 1329).

Molybdenum silicide $MoSi_2$, sp.gr. 6·2 (Defacqz, *ibid.* 1907, 144, 1424).

Tungsten silicide WSi_2, sp.gr. 9·4 (*ibid.* 848), and **Uranium silicide** USi_2, sp.gr. 8 (*ibid.* 1908, 147, 1050) have been prepared by direct union of the elements, or by reaction of the oxide with silicon, in the electric furnace.

Manganese silicides. Indefinite products, containing 0·6–13 p.c. of silicon, were obtained by Wöhler (Annalen, 106, 54).

Mn_2Si is obtained by heating together (1) quartz, manganese dioxide, and carbon, (2) silicon and manganese dioxide, (3) silicon and manganese, in the electric furnace (Vigouroux, Compt. rend. 1895, 121, 771); and also by fusing an alloy of copper and silicon with manganese in the electric furnace (Lebeau, *ibid.* 1903, 136, 89). The product is purified by extracting with nitric acid, and then 10 p.c. soda, yielding lustrous prisms, sp.gr. 6·4, decomposed by dilute hydrochloric acid. MnSi, found by Carnot and Goutal in the residue left after the action of sulphuric acid on ordinary castings (Ann. des Mines, 1900, [ix.] 18, 271), is obtained as above, using a larger proportion of silicon. Lustrous, tetrahedral crystals, sp.gr. 5·9, only slowly attacked by hydrochloric acid (Lebeau, *l.c.*; Ann. Chim. Phys. 1904, [viii.] 1, 553). $MnSi_2$ is obtained by still further increasing the proportion of silicon, as octahedral crystals, sp.gr. 5·24 (Lebeau, *ibid.* 1903, 136, 231).

The freezing-point curve for Mn, Si, shows two maxima, corresponding to Mn_2Si and MnSi respectively (Doerinckel, Zeitsch. anorg. Chem. 1906, 50, 117).

Iron silicides. Silicon is almost always present in cast iron, owing to reduction of silica in smelting. In white cast iron the amount is usually 0·1 to 0·5 p.c., and in grey 0·5–3 p.c.

Fe_2Si, first described by Hahn (Annalen, 129, 57), is obtained by heating iron with one-tenth its weight of silicon, or ferric oxide with excess of silicon, in the electric furnace. After extracting with nitric acid (1 : 4) small magnetic prismatic needles remain, sp.gr. 7 (Moissan, Compt. rend. 1895, 121, 621). It is also produced by Lebeau's method, *v.* Mn_2Si, and Compt. rend. 131, 583, and by the action of silicon chloride on iron at white heat (Vigouroux, *ibid.* 1905, 141, 828).

FeSi was obtained by Vanzetti (Gazz. chim. ital. 1906, 36, i. 498) as a button on heating a mixture of coke, sand, and lime to 3000°.

The existence of Fe_2Si and FeSi is confirmed by the freezing-point curve (Guertler and Tammann, Zeitsch. anorg. Chem. 1905, 46, 163), and by the magnetic attraction curve (Jouve, Compt. rend. 1902, 134, 1577).

$FeSi_2$ (de Chalmot, Amer. Chem. Soc. 19, 118; Lebeau, Compt. rend. 1901, 133, 1008) and $FeSi_3$ (Naske, Chem. Zeit. 1903, 27, 481) are also said to exist, but only in presence of excess of silicon. Fe_3Si_2 and Fe_5Si_2 are not definite compounds (Carnot and Goutal, Compt. rend. 125, 148; Jouve, Bull. Soc. chim. [3] 25, 290). Cementation with silicon takes place at 950° (Lebeau, Bull. Soc. chim. 1902, 27, 44).

Crystalline silicon displaces carbon almost completely from cast iron as graphite (Moissan, Compt. rend. 1894, 119, 1172).

Nickel silicides. Ni_4Si is obtained by the action of silicon chloride upon nickel, and on prolonged action of the chloride is changed to Ni_2Si (Vigouroux, Compt. rend. 1906, 142, 1270). Guertler and Tammann (Zeitsch. anorg. Chem. 1906, 49, 93) from the Ni—Si freezing-point curve, infer the existence of Ni_3Si, Ni_2Si, Ni_3Si_2, NiSi, and Ni_2Si_3.

Cobalt silicides. Silicon chloride passed over metallic cobalt at 1200°–1300° yields Co_2Si (Vigouroux, Compt. rend. 1906, 142, 635). CoSi, $CoSi_2$, $CoSi_3$, and Co_3Si_2 are also said to exist (Lewkonja, Zeitsch. anorg. Chem. 1908, 59, 293).

Palladium silicides. PdSi, obtained in small brilliant bluish-grey fragments of sp.gr. 7·3, is the only silicide isolated, but the Pd–Si freezing-point curve gives two maxima, at 1400° and 990°, corresponding to $SiPd_2$ and SiPd respectively (Lebeau and Jolibois, Compt. rend. 1908, 146, 1028).

Platinum silicides. PtSi is formed by direct union of platinum and silicon. Crystallised from molten silver-silicon alloy, the latter being subsequently removed by successive treatment with sodium hydroxide and nitric acid, it is obtained in fine prismatic crystals, sp.gr. 11·63, m.p. about 1100°. After heating with tin, and extracting with potassium hydroxide, a residue of Pt_2Si is left (Lebeau and Novitzky, Compt. rend. 1907, 145, 241; *v.* also Vigouroux, *ibid.* 1907, 145, 376). $PtCu_2Si$ results on heating platinum and copper silicides together.

A number of the silicides above mentioned may be prepared by heating the oxide of the metal with silicon carbide (Baraduc-Muller, Rev. Met. 1910, 7, 657).

The constitution of certain silicides is discussed by Manchot (Annalen, 1905, 342, 356; 1907, 357, 129).

SILICON BRONZE *v.* TIN.

SILK. Silk consists of a continuous thread produced by a caterpillar, the silkworm, to form the cocoon in which it envelops itself before entering the pupal state. There are several kinds of silkworms, all of which are included in the natural order *Lepidoptera.* The mulberry-feeding silkworms belong to the family *Bombycidæ*, and the other kinds to either the *Saturnidæ* or the *Eupterotidæ.* The silk of the *Bombycidæ* is usually termed 'true silk,' whilst the other varieties are spoken of as 'wild silks.' Those races which complete the life-cycle only once a year are said to be univoltine, whilst those which pass through the cycle more frequently are known as bi-, tri-, quadri-, or multi-voltine. The cocoons of the univoltine varieties are, as a rule, greatly superior to those of the other kinds. Among the wild silkworms may be mentioned: *Attacus ricini*, the Eri variety of India; *A. Cynthia*, the Ailanthus variety of China and India; *Antheraea yama-mai*, the oak-feeding silkworm of Japan; *A. assamensis*, the Muga worm of Assam; *A. mylitta*, the Indian tussah worm; *A. pernyi*, the Chinese tussah worm; and various species of *Anaphe*, the wild silkworms of Africa which form curious nests or aggregations of cocoons.

The fluid which gives rise to the silk fibre is formed in two glands in the body, and is exuded through two ducts or openings in the head of the caterpillar into a common orifice. The viscous streams there become coated with another secretion which flows from two other symmetrically placed glands and thus become cemented together into a double strand. On emerging into the air the fibre coagulates and becomes a firm, continuous filament, the 'bave,' composed of the two parallel strands, each of which is known as a 'brin.' When the young moth emerges from the pupa or chrysalis, it softens the end of the cocoon immediately in front of its head by the emission of a liquid, and then forces its way out. In thus effecting its egress it destroys the continuity of the fibre ; in order to obtain the silk of full length, it is, therefore, necessary to kill the chrysalis, and this is accomplished either by steaming the cocoons, submitting them to a dry heat of 70°–80°, or by freezing them.

The mulberry silkworm (*Bombyx Mori*) is probably indigenous to China, but has been introduced into almost every part of the world in which the mulberry tree (*Morus alba* [Linn.]) can be grown. It yields the best and finest silk in temperate climates, where it is usually univoltine, although sometimes it may be bivoltine. The cocoon consists of an outer, loosely woven fibre, the 'floss,' enclosing an inner, compact portion, the 'pod,' the most internal layer of which consists of a mass of closely agglutinated fibre forming a hard, gummy husk. The weight of the cocoons varies from 1 to 3 grms. About one-sixth of this is silk, of which about one-half can be unwound or reeled ; the other half, consisting of the outer floss and the inner husk, is usually combed or carded, and afterwards spun. Many of the wild silks cannot be reeled at all, and in such cases the whole of the fibre is carded and spun.

The diameter of the raw silk fibre, *i.e.* the double strand or bave, of the mulberry silkworm is about 0·020–0·025 mm., whilst that of the wild silks is usually much greater and varies from 0·040 to 0·065 mm.

Silk is a hygroscopic substance and loses 10–15 p.c. of moisture at 120°. It is a non-conductor of electricity, and is readily electrified by friction ; this sometimes renders it difficult to deal with in manufacturing operations, and may necessitate the application of glycerol or soap solution. The fibre is characterised by its exceedingly high lustre and its great strength and elasticity. It is also distinguished by the peculiar sound or 'scroop' it emits when pressed or rubbed, and to which the well-known rustle of silk fabrics is due. The density of raw silk is 1·30–1·37, and that of the degummed fibre is 1·25.

It has been shown by Städeler (Annalen, 1859, 111, 12) that the silk fibre consists of a central core of the protein *fibroin*, coated with another protein, the silk-gum or *sericin*. These substances are accompanied in raw silk by about 1 p.c. of waxy matter, a small quantity of colouring matter, and a variable amount of mineral constituents, ranging from 1 to 5 p.c. The fibroin constitutes about 70–75 p.c., and the sericin 20–25 p.c. of the dry fibre. Before silk is manufactured into textiles, it is heated in a solution of soap at 95° in order to remove the sericin, this process being known as 'boiling off' or 'degumming.' The bave becomes divided in this operation into the separate strands or brins of nearly pure fibroin, which is much softer and more lustrous than the raw material.

Fibroin is insoluble in water and organic solvents, but dissolves in concentrated solutions of alkali hydroxides, in mineral acids, in ammoniacal solutions of cupric oxide and nickel oxide, and in strong solutions of basic zinc chloride.

Sericin is a substance of a gelatinous nature ; it dissolves readily in warm soap solution or hot water, and the solution on cooling forms a jelly even when as little as 1 p.c. of the substance is present. On adding alcohol to a hot solution of sericin, the latter is precipitated as a white powder.

These proteins differ from keratin (the protein of wool, hair, &c.) in being free from sulphur. The products of their hydrolysis were first studied by Cramer (J. pr. Chem. 1865, 96, 97), who obtained serine from sericin. Weyl (Ber. 1888, 21, 1407) found that if alcohol is added to a solution of silk-fibroin in cold, concentrated hydrochloric acid, a precipitate is produced which he termed sericoin. Fischer and Bergell (*ibid.* 1903, 36, 2592) have shown that if fibroin is left in contact with strong hydrochloric acid for about 24 hours, alcohol no longer causes the formation of a precipitate, and that on evaporating the solution in a vacuum a residue is obtained containing the hydrochloride of a peptone. When this peptone is digested with trypsin it loses tyrosine and becomes converted into glycyl-*d*-alanine. Fischer and Abderhalden (*ibid.* 1907, 30, 574) subsequently isolated another dipeptide, glycyl-*l*-tyrosine, and a tetrapeptide, consisting of two glycine, one alanine and one tyrosine residues ; this tetrapeptide, on partial hydrolysis, yielded glycyl-*d*-alanine and glycyl-*l*-tyrosine. Abderhalden (Zeitsch. physiol. Chem. 1911, 72, 1) obtained a tripeptide from the hydrolysis of fibroin, viz. *d*-alanyl-glycyl-*l*-tyrosine, which was probably formed from the tetrapeptide.

Abderhalden and his co-workers have carried out a series of hydrolyses with the object of ascertaining whether the fibroins of different kinds of silk from different sources and from different insects show differences in composition. The results of these investigations are stated in the table, page 684, the figures representing percentages of dry silk fibroin after deducting the ash and the non-hydrolysable portion.

Abderhalden (Zeitsch. physiol. Chem. 1911, 74, 427) has shown that Anaphe silk, on hydrolysis, yields a relatively large proportion of tyrosine and considerable quantities of glycine and alanine ; aspartic and glutamic acids are also produced, together with traces of leucine and proline. The composition of this silk is therefore similar to that of the other varieties.

It is evident from these results that silk-fibroin is mainly composed of three amino acid residues, viz. those of glycine, alanine, and tyrosine, whilst the other constituent amino acids are present in relatively small proportions. The fibroins of the various kinds of silk possess a close similarity, but are not identical. Some varieties, such as Italian silk, yield large quantities of glycine, whilst silks of the wild types, such as the tussah silks, give a much smaller proportion of this substance.

The hydrolysis of sericin has been studied by Fischer and Skita (Zeitsch. physiol. Chem. 1901, 33, 221), and more recently by Abderhalden and Worms (*ibid.* 1909, 62, 142) and Strauch (*ibid.* 1911, 71, 365), who obtained the following results which show that the composition of this protein differs greatly from that of fibroin.

HYDROLYSIS OF SILK-FIBROIN.

—	From Italian silk (Fischer and Skita, Zeitsch. physiol. Chem. 33, 177)	From New-Chwang silk (Abderhalden and Rilliet, *ibid.* 1909, 58, 337)	From Canton silk (Abderhalden and Behrend, *ibid.* 1909, 59, 236)	From Shantung Tussah silk (Abderhalden and Brahm, *ibid.* 1909, 61, 256)	From Bengal silk (Abderhalden and Sington, *ibid.* 1909, 61, 259)	From Niet ngō tsam silk (Abderhalden and Brossa, *ibid.* 1909, 62, 129)	From Indian Tussah silk (Abderhalden and Spack, *ibid.* 1909, 62, 131)	From Tsai-tsao-tsam silk (Abderhalden and Schmid, *ibid.* 1910, 64, 460)	From Chefoo silk (Abderhalden and Welde, *ibid.* 1910, 64, 462)	From Italian silk (Roose, *ibid.* 1910, 68, 273)	From Haruko silk (Suwa, *ibid.* 1910, 68, 275)
Glycine . .	36·0	19·7	37·5	14·5	30·5	24·0	9·5	25·2	12·5	33·5	35·0
Alanine . .	21·0	23·8	23·5	22·0	20·0	18·5	24·0	18·2	18·0	20·0	22·6
Leucine . .	1·5	1·6	1·5	1·0	1·2	1·2	1·5	0·9	1·2	0·75	0·7
Serine . .	1·6	1·0	1·5	1·8	1·75	1·5	2·0	1·2	1·0	1·9	0·7
Aspartic acid .	present	2·9	0·75	1·0	0·8	2·0	2·5	2·1	2·0	1·0	1·0
Glutamic acid .	nil	1·7	not detected	1·75	trace	3·0	1·0	2·0	2·0	0·25	0·07
Phenylalanine .	1·5	1·2	1·6	1·0	1·4	1·0	0·6	1·0	1·0	1·2	1·3
Tyrosine .	10·5	9·8	9·8	9·7	10·0	7·8	9·2	7·8	8·5	9·0	9·7
Proline . .	present	1·85	1·0	2·5	1·0	1·2	1·0	1·0	2·5	0·8	0·7

Hydrolysis of Sericin or Silk-gum.

	From Canton silk (Abderhalden and Worms).	From Indian Tussah silk (Strauch).
Glycine . .	1·2	1·5
Alanine . .	9·2	9·8
Leucine . .	5·0	4·8
Serine . .	5·8	5·4
Aspartic acid .	2·5	2·8
Glutamic acid .	2·0	1·8
Phenylalanine .	0·6	0·3
Tyrosine . .	2·3	1·0
Proline . .	2·5	3·0

For further information on silk reference should be made to Matthews' Textile Fibres. E. G.

SILK, ARTIFICIAL, LUSTRA CELLULOSE, or **CELLULO-SILK.** These products are in practice prepared from solutions of organic colloids such as cellulose, and for the chemistry of their preparation reference must be made to the general article on CELLULOSE in Vol. I.

History.—In 1734 Réaumur suggested the manufacture of filaments to take the place of those produced by the silk worm. In 1855 Andermars actually patented the production of such threads or filaments from a solution of nitrocellulose (Eng. Pat. 283, 1855). A steel point was dipped into the solution, and a thread drawn from the liquid. The thread was connected with a winding machine by which it was drawn out until the liquid was exhausted.

In 1882 Weston claimed the denitration of nitrocellulose, using such reagents as ammonium sulphide for that purpose (Eng. Pat. 4458, 1882).

In 1884 the first workable process was protected by de Chardonnet (Fr. Pat. 165349). The apparatus as originally used is shown in a photograph published in a book by Filtzer in 1903.

In this process jets take the place of the steel point, the solution being forced through them at great pressure into warm air. Fine filaments may be drawn off under these circumstances and the solvent (alcohol-ether) partly recovered from the air.

Du Vivier in 1889 produced a product which was practically identical with that of de Chardonnet. In 1892 Lehner also patented certain modifications, and claimed to be able to work with much lower pressure at the jets (Fr. Pat. 221901).

As the result of these investigations yarns made in this manner came into the market and were used for the production of braids, &c., and at Besançon in France, Tubiz in Belgium, and in Germany, Switzerland, and Hungary, this product was manufactured in increasing quantities. An attempt to work this process in this country failed.

Since that time many improvements in the manufacture of filaments by this process have been devised, and some of them were patented.

These have been connected with the solution of nitrocellulose, the formation of the threads, subsequent denitration which is necessary to render the yarn less inflammable, the recovery of the solvent, and in other details. The filaments as spun are combined together into threads of a suitable size, and 'thrown' or spun in order that the threads may act properly in the subsequent working.

These yarns or threads resemble in many ways silk. They are extremely lustrous, and in some ways have been considered to be superior to the real article. They are inferior in strength and lack 'covering power,' as a result of which they have a lower value when woven into fabrics. In the manufacture of braids, trimming, &c., this defect is not noticed, or is counterbalanced by the special effects produced.

Chardonnet silk filaments have a mean diameter of $35/\mu$, a true elasticity of 4–5 p.c., a percentage elongation under breaking strain of 15–17 p.c., and a sp.gr. 1·49.

The effect of denitration on the strength of the filaments has been given as follows—

Nature of filament	Breaking Strain	Elasticity
100 denier nitrocellulose thread .	150 grms.	23 p.c.
,, after denitration	110 grms.	8 ,,
,, in wet state	25 grms.	—
Real silk .	300 grms.	18 p.c.

According to Dulitz (Chem. Zeit. 1910, 34, 989) it is impossible to completely denitrate the threads without a virtual destruction of their qualities. In practice it is arranged that the yarn contains about 0·05 p.c. nitrogen, but this must be equally distributed over the fibre. To obtain this result many factors in the manufacture of the silk itself have to be considered. These include uniformity of composition, percentage of moisture, and a uniform shrinkage on drying. When hyposulphides are used a new bath is more active than an old one. Many other details have not been disclosed.

The actual process is a difficult one to control. The temperature of the bath has a great effect on the result. This process, which when properly conducted hardly decreases the lustre of the thread, is followed by a bleaching bath. When finally finished the product possesses a beauty and gloss which has hardly been equalled by other and more recent makes, and probably accounts for the fact that it has survived and is in use at the present time.

This original process of manufacture has now to compete with others working in a more direct manner, in which the cellulose itself is dissolved, and the nitration and denitration processes dispensed with. The solvents are more easily handled and are cheaper to use. Aqueous solutions have taken the place of air as a medium for squirting into. In some cases these may act chemically on the solvents in such a way that the cellulose is thrown out of solution.

Dealing with the more important of these recent processes, in their historical sequence, Wynn and Powell, in 1884 (Eng. Pat. 16805, 1884), used a solution of zinc chloride as a solvent for cellulose. This solution was expressed into a solution—say alcohol—which removed the solvent. The cellulose was precipitated in the form of filaments which could, under certain circumstances, be collected, and after treating in other ways, dried.

These have been greatly used in the past for the production of filaments for carbon lamps. Modifications in this process were proposed by Dreaper and Tompkins, and Bronnert respectively; but this process has never been used on any scale for the production of filaments for textile purposes.

Six years after Wynn and Powell had filed their specification Despeisses (Fr. Pat. 203741, 1890) provisionally protected a process in which the cellulose was dissolved in an ammoniacal solution of copper, and then squirted into a solution which would, by acting chemically, precipitate the cellulose in the required manner. Owing to the death of the inventor the patent was never completed, but a patent on similar lines was taken out in 1897 by Pauly. Many others have followed dealing with details in the manufacture, variations in the solutions used for precipitation, use of special copper salts such as copper carbonate, in detail in the machinery used, and special treatment of the threads produced.

It is difficult to state the relative value of the different suggestions. Generally speaking, the solutions used to precipitate the cellulose are either acid or alkaline in their nature. The addition of substances like dextrose has been suggested to facilitate working conditions. The cellulose has been treated before solution with caustic soda to facilitate the process. Fremery and Urban have suggested many modifications which deal with the treatment of the threads after formation, and in the subsequent drying operations.

The third process, which is at present meeting with particular success, entails the use of cellulose thiocarbonates, which were discovered in 1892 by Cross, Bevan and Beadle. By spontaneous decomposition cellulose is regenerated from such a solution and thrown out in an insoluble condition. This process may take place immediately in the presence of suitable salts; and in 1903 Stearn (Eng. Pat. 1020, 1898) disclosed a commercial method of preparing filaments from this solution, using ammonium salts as a precipitating medium.

Many patents have since been taken out in connection with this process.

Attempts have been made to manufacture filaments from cellulose esters such as the acetates or formates. The former substance presents as a raw material advantages, but the high cost of manufacture and difficulties in the matter of solution, and the subsequent reprecipitation in the required form are very great. The substance is water resisting, and special conditions have to be observed in dyeing these filaments.

A cellulose acetate product has been tested by Herzog (Chem. Zeit. 1910, 34, 347). The average diameter equals 42·3μ.

It is soluble in cold acetic acid, coloured yellow by sulphuric acid, and iodine, and also by zinc chloride and iodine. It does not swell in water, and has a low density, viz. 1·251.

Filaments and threads have also been prepared from gelatin and casein, but little has been heard of their production on a commercial scale.

Directly connected with the manufacture of these yarns is the question of the recovery of the solvents used, and also of the materials used for precipitation. In some processes this is an essential condition to commercial success.

Reference to many patents will indicate that the machinery used in the different processes varies greatly, and is in some cases of a complicated nature. Mention might here be made of the patents dealing with the production of very fine filaments, as proposed by Thiele, where conditions of working are such that these filaments can be prepared commercially.

Machinery. Each process has its requirements as regards the machinery employed, and these have been met in various ways. The same process working in different countries differs materially in actual methods. There is also a mass of detail, which in many cases is not protected in any other way than that of secret working, and may be confined to the working of a single factory. One or two cases which illustrate the methods adopted in the manufacture of these threads may be considered.

The first case is that of the original Chardonnet apparatus. This is of interest as showing in the original patent (Eng. Pat. 2211, 1886) the apparatus already available at that time. The thread passed through a jet, which had a bore of $\frac{1}{20}$–$\frac{1}{5}$ mm., through a very short column of water and then on to the winder. When a thread broke, the broken end was seized by pincers and carried over guides to the reel to be wound. The pinions still ascending are cleaned by a rapidly revolving brush, before they descend again to pick up any more broken ends. This movement was repeated several times a minute. Air heated to 85°–90°F. is passed by supply and discharge conduits through the outer chamber. The volatile solvents carried off by the air might be 'condensed and removed by cooling,' and the air after warming returned to the apparatus. The Topham turbine system of collecting and spinning the threads at the same time (Eng. Pat. 23158, 1900) is a good illustration of the methods adopted to overcome certain difficulties in manipulation.

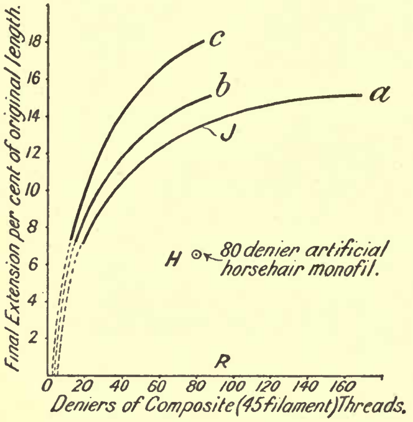


FIG. 1.

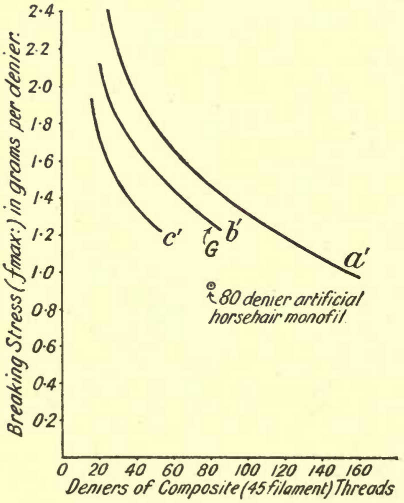


FIG. 2.

The squirted thread passes over a roller and thence into a rapidly rotating box. The fibres or threads as they are fed in are twisted together and caused by the centrifugal force to form a compact coil around the interior of the box and to be formed into hanks or skeins. If the boxes are deep, a longitudinal reciprocating movement can be given to either the box or the funnel to make sure of the even coiling of the thread in the skein form. This is a very ingenious method of combining the skeining and twisting in one operation. It is, or has been, largely used in the manufacture of artificial silk. It reduces the strain on the newly formed threads to a minimum.

A third example is that of one of the more recent patents dealing with modifications in the Thiele 'two-solution' process of spinning (Dreaper, Eng. Pat. 21872, 1908). In this case arrangements are made so that the freshly squirted thread comes in contact with a precipitating solution which acts comparatively slowly, and then passes into a stronger one, which is contained in an outer tube. The solution of cellulose flows through a delivery pipe to the jet. The weaker solution enters the inner tube and the stronger one the outer one which is attached to a vacuum pump which may be used in filling the tubes with solution to start with. The threads, after this double treatment, pass out at the lower end of the outer and longer, and are wound on to suitable bobbins or otherwise treated. These examples may be taken as illustrating the different methods in vogue. For further details the patent literature of the last ten years should be consulted.

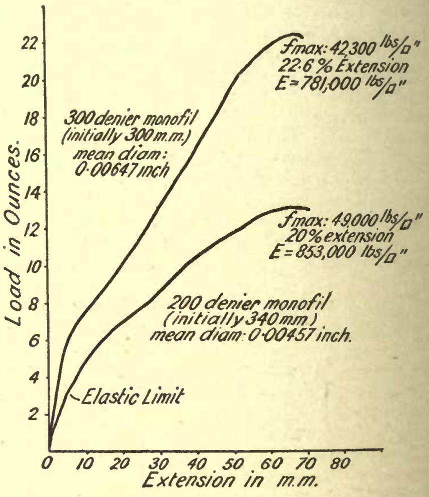


FIG. 3.

The fibres generally have specific properties which have made them useful in commerce. The extreme brightness of the yarns, which exceeds that of real silk, is probably the most important quality in the coarser counts. The ash is generally under 2 p.c., and the nitrogen varies between 0·05 and 0·13 p.c.

Strangely enough the latter refers to a 'direct' process, and the former to a nitrocellulose one. Silk contains 17 p.c. of nitrogen, so that in this way it is distinguished from the artificial silk products derived from cellulose, but not from those which may be derived from proteids, such as casein, gelatin, &c.

The method of detecting the origin of such products depends upon certain chemical tests. The diphenylamine one has generally been used in the past, and a solution of the sulphate may give the following reactions :—

Silk	Brown colouration
Tussah silk (wild)	„ but more intense
Nitrocellulose products	Intense blue
Viscose and cuprammonium products	No reaction.

Schwalbe's test with Fehling solution and one with a solution of iodine in zinc chloride are not so satisfactory. The relative action with dyestuffs is of little account in this direction.

Maschner proposes to make use of the action of concentrated sulphuric acid in the following way. 0·2 grm. of the different qualities are introduced into small Erlenmeyer flasks, which stand on white paper, and equal amounts of pure sulphuric acid, 10 c.c., are simultaneously poured over them, and the fibres thoroughly moistened by shaking. A nitrocellulose silk remains colourless, after 40–60 mins., the solution takes a pale-yellow tinge. Cuprammonium silk at once turns yellow, or yellowish-brown; the solution is yellowish-brown after 40–60 mins. Viscose silk at once turns reddish-brown, and after 40–60 mins. the solution is a rusty-brown colour.

A nitrocellulose product should show no carbonising when heated to 135°–140°. The presence of cellulose sulphuric esters which may not be removed in the denitration process may cause a complete loss of strength owing to the slow production of free sulphuric acid.

The specific gravity of the different products when compared with real silk or cellulose is as follows :—

Chardonnet	1·52
Lehner	1·51
Glanzstoff	1·50
Cellulose acetate	1·251
Natural silk	1·36
Cellulose	1·45

The normal moisture present has been given as follows : real silk, 10–11 p.c.; Chardonnet, 10·37 p.c.; Lehner, 10·71 p.c.; Glanzstoff, 10·04 p.c.

The loss of strength on wetting has been a great drawback to the use of such materials in certain directions. It must be remembered, however, that this defect is of a temporary nature, as the strength is regained on drying. This defect is gradually decreasing, and may in time be overcome. A great improvement has taken place since Strehlenert, in 1904, published the following figures :—

Yarn	Dry strength	Wet strength	P.c. loss
China silk	53·2	46·7	14·1
French (ecrue)	50·4	40·9	18·8
Chardonnet	14·7	1·7	89·6
Lehner silk	17·1	4·3	74·8
Viscose	31·5	3·5	84·0
Glanzstoff	19·1	3·2	83·0

These figures show an average loss for artificial products of 82 p.c., and for real silk of 16·4 p.c. This loss in the former case has now fallen to about 50–60 p.c. or even less.

The influence of variations in the actual size of the filaments making up the artificial silk threads on the final extension at breaking, and the breaking stress is shown in the diagrams. The general strength of these filaments is stated in grams per denier; but, as Dreaper (J. Soc. Chem. Ind. 1909, 28, 1300) has shown, this is not an entirely satisfactory manner of giving the relative strength, unless the size of the individual filaments is constant or accurately known.

Figs. 1 and 2, taken from the above communication, indicate the final extension before breaking, and the actual breaking stress of artificial threads of varying size.

Fig. 3 shows typical load-extension curves obtained with single filaments of large diameter (artificial horse-hair). The normal stress at fracture for a 200 denier thread is 49,000 lbs. per square inch, and the percentage extension is 20 p.c. It is observed that the curves in this case are characteristic of those obtained with metal wires.

Cross and Bevan have given the strength of coarse count silks as between 1·0 and 1·4 grms. per denier for artificial products, as against 2·0 and 2·5 grms. per denier for the real product. But in the counts containing finer filaments this may be exceeded in the former case. The term 'elasticity' as applied to these filaments in a composite thread is not valid, as other factors also enter into this figure. A practical trial is necessary before the value of any individual product can be obtained from the point of view of weaving or actual wear. 1000 metres of thread of a weight of 0·1 grm.=1 denier, and so on.

The size of the actual filaments making up the threads is a matter of great importance. If they are of large size the silk may have a harsh feel, but it will probably be very bright. When threads are required for weaving purposes it is necessary that the filaments be of less diameter. This also gives softness and increased strength. It is possible to spin these very much finer than those of the natural article.

The relative diameter of the filaments at present on the market varies not only with the different makes, but according to the requirements and uses to which the yarns are put. The following figures represent the variations noticed in certain cases—

Nature of materials	Size in microns
Chardonnet	35–100
Lehner	40–132
Pauly	40–70
Viscose	35–60
Thiele	7–15
Gelatin	60–85
Real silk	10–15

(A micron = 0·001 mm.).

Many attempts have been made to improv the water-resisting qualities of these products. The most successful method put forward is that known as the Sthénose treatment. The silk is subjected to the action of formaldehyde, which, according to Escalier, leads to a condensation of the cellulose molecule and gives greater strength both in the dry and wet state, but specially in the latter.

Quality	Size	Tenacity (wet)	Tenacity (dry)
Sthénose	130 den.	208	140
Viscose	130	146	38
Givet	120	130	39·5
Chardonnet	90	144	39·6

These figures certainly indicate an increase in strength as present both in the dry and wet state after this treatment.

Certain difficulties have been experienced in the past in dyeing these filaments and threads. Different makes of artificial silk react in different ways in this respect. The nitrocellulose product will not stand so severe a bleaching as the hydro-cellulose products.

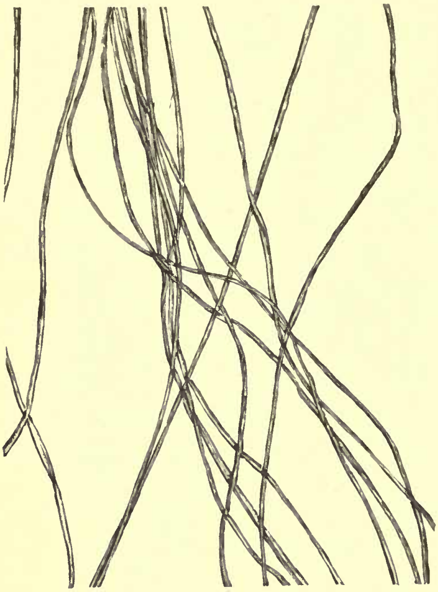


FIG. 4.

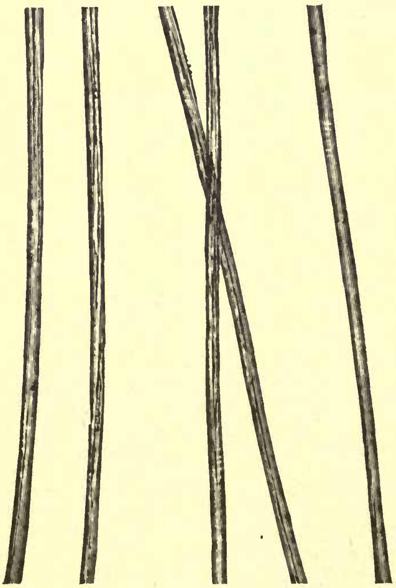


FIG. 5.

Special colour effects may be obtained by taking advantage of the different dyeing properties of these materials as compared with natural fibres when they are present together in fabrics.

The 'feel' of these yarns is improved by a passage through a weak acid bath as in the case of silk itself.

The world's output of these yarns has been variously estimated as between 8–10,000 tons per annum. The output of real material in the yarn state is about 50,000 tons, so that the output of the artificial product is likely to still further increase, especially as some of the products are now being used in large quantities in the weaving of fabrics. It is difficult to obtain figures giving the relative output of these yarns as made by the different processes in vogue, but the output of the nitrocellulose product is rapidly decreasing and that of the viscose product increasing. The future of the cupro-ammonium process may depend upon certain factors which are not yet thoroughly realised.

Figs. 4 and 5 illustrate the relative nature of fine and coarse count artificial fibres enlarged to 80 diameters. W. P. D.

References: Nitrocellulose Industry, Vol. I. 1911, by Worden; Die Künstliche Seide, by Suvern; Fabrikation de la soie artificielle, by T. Foltzer; Matthews, Textile Colourist, 27, 322; Dreaper, J. Soc. Dyers Col. 1907, 23, 7; J. Soc. Chem. Ind., 1909, 28, 1300; E. Berl., Chemiker Zeitung. 1910, 34, 532, and many other references which may be found in Worden's 'Nitrocellulose Industry,' vol. i. 1911.

SILK GREEN. *Chrome green v.* CHROMIUM.

SILOXICON. A by-product obtained in the manufacture of carborundum consisting mainly of a substance of the formula Si_2C_2O, *v.* SILICON.

SILUNDUM. A carbon silicide obtained by heating carbon with carborundum, to which sand is added, at a temperature of 1700°–1800°.

SILVER. Ag (*Argentum*). At.wt. 107·88. The knowledge of this metal dates from the remotest antiquity, and the earliest records refer to its use as a medium of exchange.

Properties.—In colour silver is whiter than any other common metal or alloy, and it is capable of receiving a brilliant polish. When in the form of fine powder, as, for instance, when the chloride has been reduced by iron and acid, silver is grey and earthy in appearance. A thin film of silver is blue by transmitted light. It crystallises in the cubic system and small octahedra are occasionally observed. The tenacity of silver wire of 1 square mm. in sectional area is equivalent to 17·27 tons per square inch at 0°. It is more malleable and ductile than any other metal except gold, and may be hammered into leaves 0·0025 mm. thick. It is hardened by hammering or rolling, but its softness is restored by annealing at about 200° C. It is harder than gold but softer than copper. It is the most perfect conductor of heat and electricity known, and has therefore been adopted as the standard for comparison. Its conductivity is increased by annealing. Its sp.gr. after having been cast is 10·50, and this is only slightly altered by rolling or annealing. Solid castings of pure silver are, however, difficult to prepare, and a cast ingot usually contains minute cavities by which its density is apparently reduced. The sp.gr. of molten silver is 9·51. Precipitated silver has a density as high as 10·61.

Silver melts at 961·5° (Holborn and Day) and begins to volatilise in a sensible degree at about the m.p. of copper, 1081°. It can be distilled in quantity by the oxyhydrogen blowpipe in a suitable furnace, and boils vigorously in the electric arc furnace. Its vapour is pale blue. Molten silver absorbs about 22 volumes of oxygen and the whole of the gas, except 0·7 volume, is given off again during solidification. The disengagement of the gas causes effervescence and 'sprouting,' which may be prevented by the presence of oxidisable metals or by slow cooling. *Cf.* Sieverts and Hagenacker, Zeitsch. physikal. Chem. 1909, 68, 115; Donnan and Shaw, J. Soc. Chem. Ind. 1910, 29, 987.

Silver is not acted on by oxygen, whether dry or moist, except to a very slight extent at high temperatures. Chlorine is absorbed by it even at the ordinary temperature with the formation of silver chloride. The action is rapid at a red heat. Silver sulphide is still more readily formed at all temperatures. Silver is dissolved by nitric acid and by boiling concentrated sulphuric acid.

Silver ores. The following are the more important: Native silver 97–99·8 p.c. Ag; the antimonide (*dyscrasite*), Ag_2Sb–Ag_6Sb; the telluride (*hessite*), Ag_2Te; the sulphide (*argentite*), Ag_2S; brittle silver ore (*stephanite*), $5Ag_2S,Sb_2S_3$–68·3 Ag; dark-red silver ore (*pyrargerite*), $3Ag_2S,Sb_2S_3$–60Ag; light-red silver ore (*proustite*) $3Ag_2S,As_2S_3$–65·4 Ag; *polybasite* $(Cu_2S,Ag_2S)_9(Sb_2S_3,As_2S_3)$–64–72 Ag and 10–3 Cu; fahl ore (grey copper ore), either a complex antimonio-sulphide, arsenio-sulphide, or antimonio-arsenio-sulphide, containing variable quantities of silver, occasionally exceeding 30 p.c.; *stromeyerite* Cu_2S,Ag_2S–53·1 Ag; *horn silver* AgCl; the iodide and bromide; and amalgams of varying composition.

Most ores of lead contain silver; indeed, this metal is of such constant occurrence with lead, that ores of the latter metal form one of the main sources of production of silver. Silver is also frequently present in ores of zinc and copper, and considerable quantities of the precious metal are annually derived from this source. It is also found occasionally in ores of iron, nickel, cobalt, and bismuth.

Extraction of silver from ores. The processes of silver extraction are very varied, owing chiefly to the diversity of the ores to be dealt with. The methods may be classified under the following heads:—

1. Amalgamation;
2. Lixiviation;
3. Smelting, with subsequent separation of the silver from metallic lead or copper.

For the parting of silver from gold in bullion, *see* GOLD.

AMALGAMATION OF SILVER ORES.

It has long been known that silver cannot be extracted from its ores by amalgamation so readily as gold, on account of its lower density and its habit of being in combination. Silver ores yield only small percentages of their silver contents when crushed in stamp batteries and allowed to flow over amalgamated tables. Prolonged contact with mercury is required and some of the compounds of silver must be previously decomposed. Mercury reduces metallic silver from the chloride, bromide, iodide, and sulphide, and forms an amalgam with the reduced metal, but the action on the sulphide is very slow. Other compounds of silver, such as the complex sulphides containing arsenic, antimony, &c., resist the attack of mercury, and are converted into silver chloride before amalgamation by roasting the ore with common salt, or by the slow action of common salt and copper compounds at the ordinary summer temperature, as in the patio process.

The *patio process* was invented in Mexico in 1557 and was still in use there in 1908, but is stated to have been abandoned subsequently in favour of the cyanide process. The ore was coarsely crushed by stamps (*see* GOLD) or otherwise, and then ground with water in *arrastras* or circular stone floors round which were dragged stones attached to horizontal arms rotating round a central axle. The finely-ground ore was then transferred to a well-paved *patio* or amalgamating courtyard, where it was mixed with mercury, common salt, and *magistral*, a mixture of copper and iron sulphates produced by roasting copper pyrites. The mixing was usually effected by the trampling of mules. The ore-heap or *torta* was kept wet, but an excess of water was avoided. The reactions are complicated and have given rise to much discussion. According to Vondracek (Revue de Metallurige, 5, 1908, 678) cupric, cuprous and ferric chlorides are formed and these decompose the silver sulphides with the formation of silver chloride, which is reduced by mercury. Some of the reactions may be represented as follows:—

$$Ag_2S+CuCl_2=2AgCl+CuS$$
$$Ag_2S+Fe_2Cl_6=S+2AgCl+2FeCl_2$$
$$2Ag_3AsS_3+3CuCl_2=6AgCl+3CuS+As_2S_3$$
$$2AgCl+2Hg=Hg_2Cl_2+2Ag.$$

The period of amalgamation in the *torta* usually lasted from 2 to 4 weeks. The mixture was then stirred with water in tanks and the amalgam, settling to the bottom, was collected, strained through filter bags to separate the excess of mercury, and retorted. Many ores yielded about 75 p.c. of their silver under this treatment.

In the old *cazo* or *caldron process*, surface ores containing native silver, silver chloride, &c., and little or no sulphide were boiled and stirred with mercury and a solution of common salt in vessels consisting either entirely or in part of copper. The silver was first reduced by the copper and then amalgamated. The *Franketina* process was similar, sulphide ores being roasted with common salt and then boiled with sea-salt and mercury in wooden vessels with copper bottoms. These processes were formerly in use in South America and Mexico.

In the *Krönke process*, introduced in Chile in 1860, a hot solution of cuprous chloride dissolved in common salt is used to decompose refractory silver compounds. The ore is treated in rotating wooden barrels, and after a time mercury and lead or zinc amalgam is added, the silver being reduced to the metallic state from chloride by means of the lead or zinc. The obsolete Freiberg barrel amalgamation process was used for the treatment of sulphide ores which were roasted with salt and amalgamated in rotating barrels with mercury, iron, and water. The iron effected a saving of mercury by reducing or preventing the formation of its chlorides.

These processes were never in such wide

use as the *pan amalgamation process*, in which crushed ore is ground to slimes in iron pans and then thoroughly mixed with mercury in the same vessels. An amalgamation pan is shown in Fig. 1. It consists of a flat-bottomed circular vessel about 5 ft. in diameter with a capacity of about 1½ tons of ore to a charge. The bottom and lower part of the sides are of iron, and the upper part of the sides of wood. Through the centre of the bottom rises a hollow pillar within which is a revolving upright shaft to which are attached grinding plates or 'mullers.' These can be lowered so as to touch the bottom or raised some distance. The pan can be warmed by steam passed into the hollow bottom or jacket. The charge is run into the pan as a thick paste, and the mullers, which are already revolving, are then lowered and the pulp is ground between them and the bottom, detachable shoes and dies taking up the wear. After the pulp has been reduced to impalpable slime, the mullers are raised a little, mercury is added, and the charge is stirred for 2–4 hours longer. The consistency of the pulp is such that globules of mercury become dispersed through it without sinking to the bottom. Chemicals, such as common salt and copper sulphate, are added with the object of promoting amalgamation. These substances are supposed to act in the same way as in the patio process, but more rapidly owing to the higher temperature.

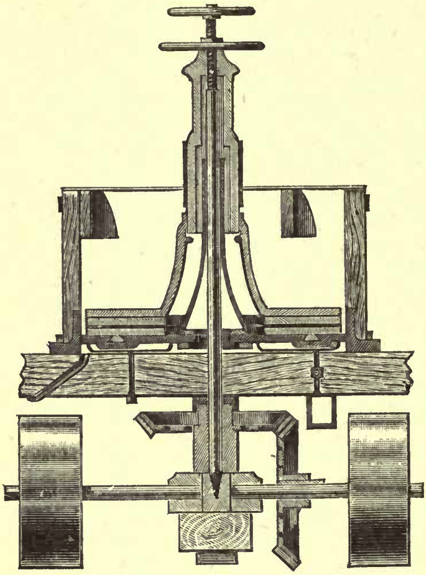


FIG. 1.

When the amalgamation is complete the speed of the mullers is reduced and the pulp is diluted by filling the pan with water. After a few minutes, the mercury, which has collected at the bottom of the pan, is drained off automatically into a sump, and the pulp is run off into the settling pan. This is similar to the amalgamating pan, but larger and provided with stirrers instead of grinding mullers. The pulp is further diluted and the lighter parts kept in suspension by stirring whilst the remainder of the mercury settles to the bottom and passes to the mercury sump, whence it is raised to the top of the building by a small ladder-bucket elevator. At intervals the silver is separated from the mercury. For this purpose the mercury is cleaned from sand, sulphides, &c., by grinding and stirring with water in a clean-up pan or barrel. The mercury is then strained through canvas, and the pasty amalgam recovered in the filter bags is retorted. The volatilised mercury is condensed under water and the residue left in the retort is melted and cast into bars.

The *Boss system* of pan amalgamation differs from that described above in being continuous in action. A number of pans and settlers are arranged in series, and the pulp from the stamp battery flows continuously through them, overflowing from each pan into the next successive one. The grinding is completed in the first pans, and the amalgamation is done in the later ones, the settlers recovering the amalgam.

Certain ores cannot be treated directly by the 'Washoe process' of pan amalgamation described above, but can be made to yield a high percentage of their silver by being roasted with common salt before being amalgamated ('Reese river process'). Silver sulphide is decomposed and silver chloride formed which is reduced to metallic silver chiefly by the iron of the pan and left in a readily amalgamable condition. The ores dealt with in this way are those containing the complex antimonial and arsenical silver sulphides and also 'dry' ores (*i.e.* those not especially suitable for smelting) containing silver sulphide mixed with sulphides of iron, copper, zinc, and lead. Ores containing large percentages of sulphides, especially galena, are usually smelting ores, and are not suitable for treatment by roasting and amalgamation. In the Reese river process, the ores are first dried, usually in furnaces similar to those used in roasting, and are crushed dry in stamp batteries or more rarely in ball or edge-runner mills. The preliminary drying before dry-crushing is required mainly to facilitate sieving.

For chloridising roasting the charge must contain some sulphide, unless MnO_2 is present in the ore. At Freiberg ores were formerly roasted with 20–30 p.c. of raw matte, but with some ores in the United States, as little as 6 p.c. of sulphide is found to be enough. An excessive quantity of sulphide gives rise to an undue consumption of salt and to avoid this, part of the sulphur is sometimes removed by roasting in air before the salt is added. The amount of salt required for roasting varies from 3 to 20 p.c., according to the ore. In the furnaces, sulphides are converted into oxides and sulphates, sulphurous and sulphuric anhydrides being given off. The sulphates and salt react, producing metallic chlorides and sodium sulphate. Chlorine and hydrochloric acid are also produced, and these act on metallic sulphides, oxides, sulphates, arsenates, antimonates, &c., yielding metallic chlorides as well as chlorides of sulphur, arsenic, and antimony.

After roasting the silver in the ore is mainly (up to 95 p.c.) in the form of chloride, which is mixed with chlorides, oxides, and sulphates of iron, copper, zinc, lead, nickel, &c. Some unaltered silver sulphide, arsenide, &c., as well as oxidised compounds of silver, are also present. The losses of silver in roasting are due to dusting and volatilisation, and vary with the form of furnace, the temperature, the current of air, the duration of the operation, and the nature of the ore. The losses of silver in a long-bedded calciner at Sonora were found by Clemes (Schnabel and Louis' Metallurgy, vol. i. 821) to be 11·6 p.c. at a dull-red heat, 13·7 p.c. at a red heat, and 15·9 p.c. at a cherry-red heat.

The furnaces used in roasting are reverberatories with hand or automatic stirring, rotating cylinders, and shaft furnaces. The automatic stirrers are usually attached to endless chains, half of which are outside the heated area. In rotating-cylinder furnaces the stirring is effected by the movement of the furnace, and the heat is supplied by flames passing through the cylinder. In some cylinder furnaces, *e.g.* Brückner and Hofman furnaces, the ore is charged in through manholes in the side of the cylinder, and the furnace is then closed and rotated until the roasting is completed, when the ore is discharged through the manholes. In White-Howell, Argall, and other furnaces, the cylinder is inclined and the ore passes through it continuously, entering at the end farthest from the fire. In shaft furnaces, such as the Stetefeldt, the ore falls in a shower through a rising current of hot air, the roasting of each particle being completed in a few seconds.

In general the ore is allowed to cool slowly, as the chloridising of the silver proceeds during cooling without increasing the loss of silver by volatilisation.

The pan amalgamation of roasted ore resembles that of unroasted ore already described. The silver chloride is reduced to metal by the iron of the pan and mullers, before the addition of mercury.

LIXIVIATION PROCESSES.

In the extraction of silver by lixiviation the silver is dissolved from its ores by aqueous solutions, and after filtration is precipitated from the clear liquid as metal or in the form of sulphide. The *cyanide process* is by far the most important of these methods. It has been applied to the treatment of silver ores in many parts of the world during the last few years, especially in Mexico, and its use has been rapidly extending. The other lixiviation processes, the patio process and pan amalgamation, have already been superseded by cyaniding at many mines.

In the following account of cyaniding silver ores, the descriptions of Mexican and American practice given by Caldecott (J. Chem. Met. and Ming. Soc. of S. A. 1908, 8, 203 and 266), C. H. Fulton (Mineral Industry, vols. 17, 18, and 19), Alfred James and others have been followed.

The ore is usually crushed very finely with cyanide solution. No preliminary roasting is required, the chloridising roasting at first practised in America having been given up. Stamp mills similar to those described under GOLD are in general use for crushing. Sometimes fine battery screens are employed and the ore crushed fine in one operation. For example, at a mill at Guanajuato there were slotted screens equivalent to wire gauze with 45 meshes to the linear inch, the duty being only 2·7 tons per day per stamp (Caldecott, *l.c.*). More often coarse screens are used in the stamp battery, and the coarsely crushed pulp is passed to tube mills (*see* GOLD), where it is for the most part reduced to impalpable slime. In some places the crushing is done by means of other grinding machines, such as Chile mills or edge-runners, in which the ore is pulverised by heavy rollers running round on their tires in iron pans. At the Mexico mill, El Oro, 40 stamps crush 200 tons of ore per day through a 16-mesh screen, and six tube mills, each 4 ft. in diameter and 20 ft. long, deal with the product. After being finely ground in the tube mills, 90 p.c. of the pulp will pass through a 200-mesh screen (Caldecott, *l.c.*).

In crushing with cyanide no amalgamated copper plates are used, but with some ores, coarse native silver accumulates in the mortar boxes of the stamp mills and is from time to time collected by hand. The pulp from the stamps, or even from the fine grinders, is, in many cases, concentrated on Wilfley tables or other machines with the separation of material from which the silver would not be readily dissolved in cyanide, and this concentrate is shipped to a smelter together with any rich hand-picked ore that may come from the mine.

After concentration, if any, and fine grinding the larger particles ('sand') in the pulp are commonly separated from the fine particles ('slime') by settlement in water with the aid of such machines as Cone classifiers (*see* GOLD), the Dorr classifier, &c. The Dorr machine consists of a settling box in the form of an inclined trough open at the upper end, in which automatic rakes keep the slimes in suspension and remove the heavy material as fast as it settles. The liquid and slime overflow at the closed end. The sand is either returned to the tube mill ('all-sliming process') or treated by percolation with cyanide solution in large vats in which filter beds form false bottoms. The sand requires a lengthy treatment with cyanide, the solution being drained off and the charge aerated at intervals to facilitate the solution of the silver. Oxidising substances ('chemical aerators') are also added to assist the aeration.

The slime treatment consists in agitation with cyanide solutions and simultaneous aeration. Stirring gear in comparatively shallow tanks was formerly used for agitation, and the treatment continued for as long as 50 hours, the rate of dissolution of silver sulphide in cyanide solutions being very slow. When the solution is separated from the ore by decantation after mechanical agitation, the process is slow and incomplete, as the pulp cannot be allowed to settle completely before decantation owing to the difficulty of again setting the paddles in motion after the addition of water for washing. The result is that the residues remain somewhat rich both in silver and cyanide, and in order to reduce these losses, mechanical filters (filter presses and vacuum filters) were introduced to complete the work begun by decantation. These have proved so successful as largely to supersede washing by decantation for silver ores in America. Further reference is made to some of these filters below.

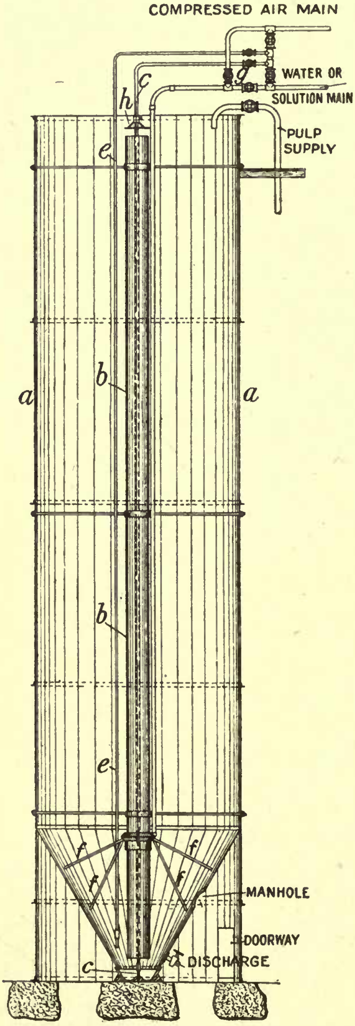


FIG. 2.

The Pachuca tank or Brown agitator making use of compressed air, is more advantageous than mechanical agitators. A sectional elevation of this agitator is shown in Fig. 2. The writer is indebted to the Cyanide Plant Supply Co., of London, E.C., for the illustration and also for the designs reproduced in Figs. 3 and 4. The Brown agitator was introduced in New Zealand in 1907, and afterwards adopted at the Pachuca mine, Mexico, whence its use spread widely. It is a steel cylindrical vat (*a*, Fig. 2) of, say, 45 ft. deep and 15 ft. in diameter. There is a pipe, *b*, in the central axis of about 1 in. diameter per foot of tank diameter, extending from near the bottom to near the top of the tank. At the bottom of the central tube compressed air is introduced from a pipe *c*, of about 1½ ins. in diameter. The air pressure is at first as much as 50–100 lbs. per square inch, but afterwards it is regulated so as to be just enough to overcome the weight of the column of water at the point of introduction. The tank is filled with pulp with a relation of solid matter to water of say 1 : 1·5, and the air turned on, by means of the valve *g*, when part of the water in the central tube is displaced by air and the centre column of material correspondingly reduced in weight The result is that the central column is pressed up by the weight of the water in the surrounding tank and the pulp is effectively agitated and at the same time aerated. The bottom of the tank is a (reversed) cone, and there are no undisturbed portions of the pulp.

The Pachuca tank is suitable both for fine sands and slimes, and the power required is far less than with mechanical stirring, being about 2¼ H.P. per 50 tons of slimed pulp, the charge in a 40 ft. by 10 ft. tank (James, Eng. and Ming. Jour. Jan. 1908, 17). Ordinary mill pulp is usually thickened by filtering off part of the cyanide solution before being charged into Pachuca tanks. The charge can be allowed to settle until the solid matter is packed down quite firmly before the air-jet is turned on. In that case water or solution is introduced through the wash-ring *f*, in order to soften the material at the bottom of the cone. With the aid of this device the pulp is soon circulating perfectly, if it is very finely ground material, not containing heavy particles of sulphide, &c. These may cause difficulties, but they have been overcome and the efficiency of Pachuca tanks increased by the introduction by A. T. Grothe of a system of continuous work, the pulp overflowing from one tank to another until the dissolution of the silver is complete, the overflow from the last tank passing to a filter (Trans. A.I.M.E. 1911, 595).

Slime from classifiers requires to be thickened, or de-watered, before it is fed into Pachuca tanks. The Dorr continuous thickener in wide use for this purpose consists of a shaft suspended vertically in the centre of a tank and carrying at its lower end radial arms, to which short pieces of angle iron are attached. When the shaft is rotated very slowly, the settled material is gradually moved to the discharge opening in the centre of the tank. The clear water overflows at the top of the tank.

The earliest of the rapid filters were filter presses in which the solution was forced through canvas by air under high pressure. These were first used with gold ores. The vacuum filters have been in use since 1903, and are very effective. In the Moore filter (Eng. & Ming. Jour. 1903, 76, 855; Trans. A.I.M.E. Sept. 1904) a vacuum filter frame is lowered into the pulp and kept immersed in it until a layer of slime of ¾–1 in. thick is formed on the surface of the canvas. The filter frame is then hoisted out and the slime-cake is washed by clear water forced through it. When the cake is free from cyanide and silver it is detached by air blown into the inside of the filter. Among other successful vacuum filters are the Butters (Ming. and Sci. Press, June 22 & 29, 1907), the Ridgway (Min. Ind. 1907, 16, 540), and the Burt (Ming. & Sci. Press, 1907, 95, 717). Fig. 3 is the plan and Fig. 4 the elevation of a vacuum filter plant (Cyanide Plant Supply Co.) of the fixed immersion type. In all these filters lime gradually clogs the canvas, and after a time is removed by a bath of dilute hydrochloric acid.

The silver is precipitated from the clear solutions either by zinc-dust or zinc shavings. Zinc dust is mixed with the solution in tanks and separated by filter pressing, but zinc shavings are contained in boxes through which the solution is allowed to flow. The solutions are less dilute in cyanide than those used for gold ores, and contain large quantities of silver, and owing to these facts coarse zinc shavings are used, not coated with lead. The zinc-silver couple, soon formed by precipitation of the silver, gives a high precipitating efficiency to the zinc and enables the lead-zinc couple to be dispensed with.

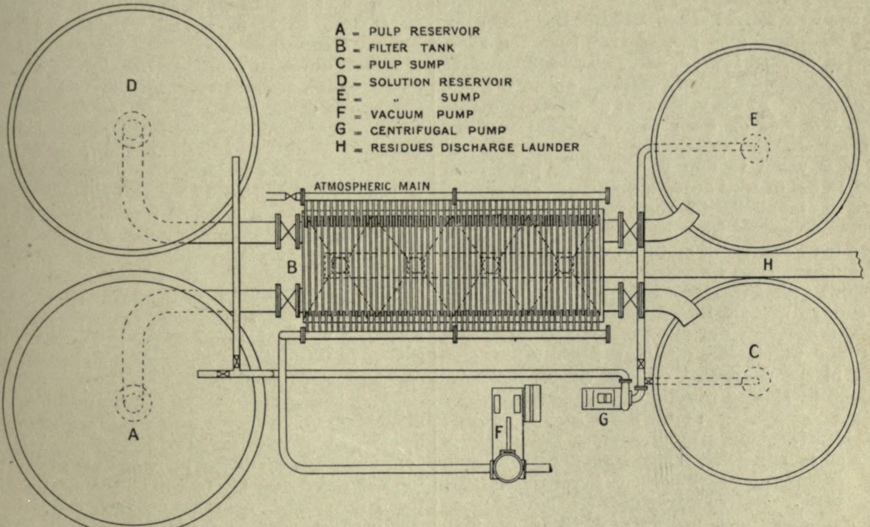

A = PULP RESERVOIR
B = FILTER TANK
C = PULP SUMP
D = SOLUTION RESERVOIR
E = " SUMP
F = VACUUM PUMP
G = CENTRIFUGAL PUMP
H = RESIDUES DISCHARGE LAUNDER
ATMOSPHERIC MAIN
D
E
B
H
C
A
F
G

Fig. 3.

In recovering the silver from the zinc boxes, simple screening of the precipitate separates the zinc and gives a product containing 50–70 p.c. of silver, which is briquetted by air pressure, partly dried, and smelted with 2 p.c. of nitre without any treatment with acid or by roasting. Large (No. 300) graphite pots or steel pots are used. The silver thus produced is somewhat impure and is sometimes refined by passing air through the molten bullion, as proposed by Rose (*see* Min. Ind. 1910, 320).

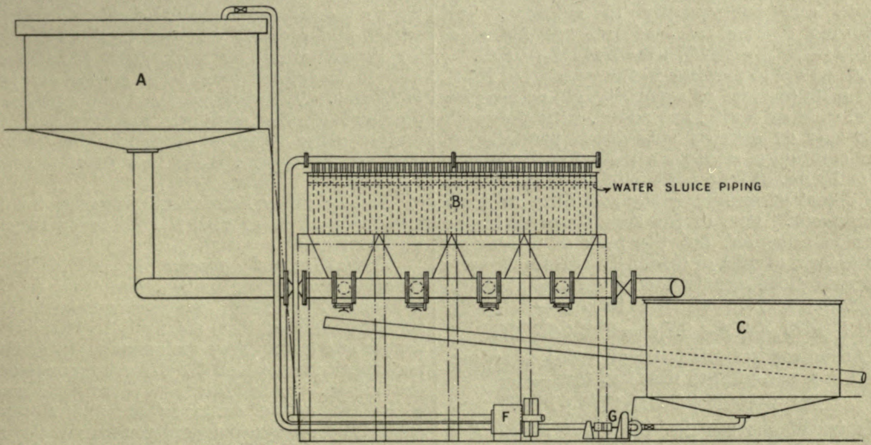

A
WATER SLUICE PIPING
B
C
F
G

Fig. 4.

The cyanide consumption on Mexican silver ores varies from 1 to 4 lbs. per ton, and 70–90 p.c. of the silver is recovered. Although power in Mexico is cheap (30*s*. per H.P. per month for transmitted electric power) and unskilled peon labour is only 1*s*. 6*d*. per day, the cost of treatment, according to Caldecott, is heavy, varying from 8*s*. to 12*s*. per ton. This is due to the high consumption of cyanide and the large amount of power required for the fine grinding in vogue.

The strength of the cyanide solutions has a considerable range. The solution used in the stamp mills contains 0·1 p.c. of cyanide upwards. At the San Rafael mine, Mexico, the mill solution contained 0·25 p.c. in 1909 (Girault, Proc. Inst. of Metals, 1910, 4, 288). The solutions for slime treatment usually contain about 0·1 p.c. of cyanide. In the treatment of sands, solutions with 0·5 p.c. or even more cyanide are not uncommon.

It is usual to add to the slime pulp from 4 to 12 oz. of lead acetate per ton of dry slimes. This is intended to remove the deleterious soluble sulphides from the solution, but doubts have been expressed as to its usefulness, on the grounds that the quantity would be insufficient without aeration, and efficient aeration should be enough without lead salts.

The chemistry of the process presents some features which are different from those met with in the treatment of gold ores. The ores treated in Mexico usually consist of hard flinty quartz containing little base metal mineral (Caldecott). The greater part of the silver is present as argentite, Ag_2S, with a little arsenic and antimony as proustite, pyrargyrite, and stephanite. Native silver and the haloid compounds sometimes occur, and these dissolve readily. Argentiferous tetrahedrite, galena, or blende when present prevent the use of cyanide unless they can be removed as concentrates.

Silver sulphide is dissolved according to the equation:—$Ag_2S+4NaCN=2NaAg(CN)_2+Na_2S$. This reaction is reversible, and in dilute solutions about 100 molecules of NaCN must be present to 1 molecule of Na_2S to prevent reprecipitation of Ag_2S. By aeration, however, the alkaline sulphide is oxidised to thiosulphate and caustic alkali, and subsequently to sulphate. The following reaction also occurs, but far more slowly:—$Na_2S+NaCN+O=NaCNS+Na_2O$.

As an aid to aeration in the removal of Na_2S, lead salts (acetate or even litharge) or mercury salts, such as $HgCl_2$, are added, with the result that lead or mercury sulphide is precipitated. The solution is strongly alkaline, as in Mexico 20 or 30 lbs. of lime per ton of ore is used, with the object of increasing the solubility of silver compounds. Part of the lime dissolves in the cyanide solutions, but the bulk of it remains in the form of milk of lime. The alkali converts litharge or lead acetate into an alkaline plumbite (K_2PbO_2), and this reacts as follows—

$$K_2PbO_2+K_2S+2H_2O=PbS+4KOH.$$

According to Caldecott lead oxide is regenerated in a well-aerated solution, thus—

$$PbS+NaCN+O=NaCNS+PbO.$$

This would account for the great effect of a few ounces of lead salts per ton of ore in which some hundreds of ounces of silver sulphide may be present.

It was found by Holt (Ming. & Sci. Press, 98, 546; 99, 159) that if the silver is present in the form of proustite (Ag_3AsS_3), pyrargyrite (Ag_3SbS_3), or tetrahedrite (fahlore), the presence of lead salts in addition to lime seems to retard rather than assist dissolution. These minerals yield their silver to cyanide satisfactorily only if subjected to a chloridising roast. Manganiferous silver ores are also generally refractory to cyanide.

A combination of amalgamation and cyaniding applied to certain ores in Mexico is described by Brodie (Mex. Ming. J. 1911, 12, 21; J. Inst. of Metals, 1911, 5, 297). The ores contain galena, blende, and pyrite, and various amounts of silver, down to 4 oz. per ton, in the form of native silver, argentite and arsenical silver. The high-grade ore is crushed direct by stamps, and some native silver remains in the mortar and is collected from time to time. The pulp is then amalgamated in 4 ft. pans, the charge consisting of 1000 lbs. of ore, 15–17 lbs. of mercury, 45 lbs. of sodium cyanide, 4 oz. of lead acetate, 3½ lbs. lime and stock solution to make a 1 : 1 pulp.

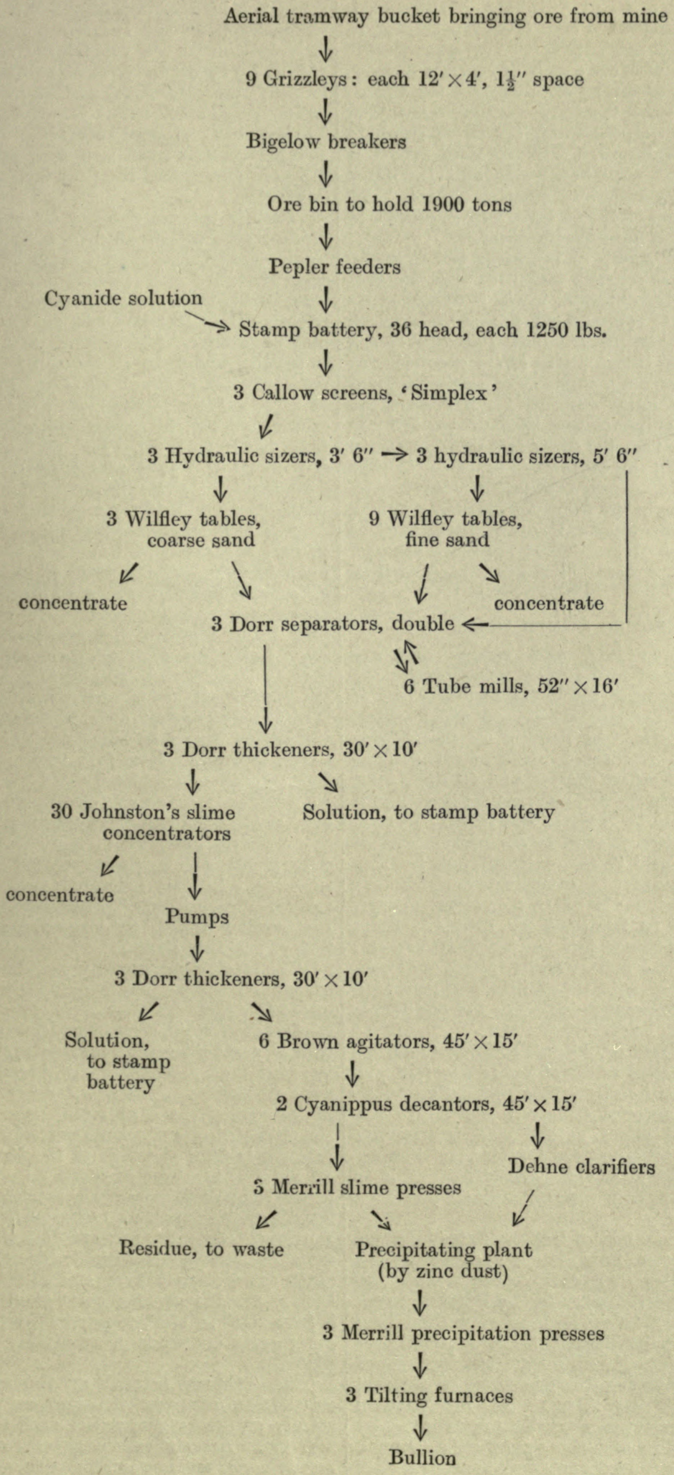
Grinding without mercury is carried on for 6 hours, followed by 10 hours' mixing with mercury. The charge is then transferred to a settler where it is leached and agitated mechanically and by compressed air for 12 hours. After this it is washed free from mercury, thickened, and treated in Pachuca tanks.

The low grade ore is concentrated in the ratio of 50 : 1, and the concentrates are separated into rich and poor material. The rich concentrates are amalgamated as described above but for 2–5 days, and treatment in the settler lasts for 6 days, with decantation each day. Then the product goes to the Pachuca tanks. The poor material is leached in percolating tanks with cyanide (50 lbs. per ton of concentrates), lime and lead acetate. The charge is treated by percolation for 12 hours and then the liquid is drained off and the charge aerated for 12 hours. This alternate treatment is continued for two months or until 95 p.c. of the silver has been extracted.

The system of treatment of silver ores by cyanide now adopted is complicated, as is illustrated by the following abridged 'flow sheet,' which was recently designed (and kindly lent for reproduction) by Mr. Alfred James for a mill to be erected by a large mining company in Mexico. The abridged sheet is simplified by omission of the sampling arrangements and certain other features which form an essential part of the design. The flow sheet is shown opposite.

Among other lixiviation processes for the treatment of silver ores the following may be mentioned:—

The *Ziervogel process* is applicable to argentiferous copper mattes, free from As, Sb, Bi, and Pb. These mattes are formed in smelting and consist chiefly of sulphides of copper and iron. They are now usually smelted for copper, from which the silver is separated by electrolysis. In the Ziervogel process the matte is roasted in an oxidising atmosphere at a gradually increasing temperature with the formation of sulphates. Sulphate of iron is formed first together with some oxides of iron and copper. At a temperature of about 700°, however, the iron sulphate is decomposed, sulphur dioxide and oxygen are evolved and copper sulphate is produced. Then as the temperature rises $CuSO_4$ is converted into $2CuO{\cdot}SO_3$ at 740°, and into CuO at 840°–850° (Friedrich, Metallurgie, 1910, 7, 323). At


Aerial tramway bucket bringing ore from mine
9 Grizzleys: each 12′×4′, 1½″ space
Bigelow breakers
Ore bin to hold 1900 tons
Pepler feeders
Cyanide solution
Stamp battery, 36 head, each 1250 lbs.
3 Callow screens, 'Simplex'
3 Hydraulic sizers, 3′ 6″
3 hydraulic sizers, 5′ 6″
3 Wilfley tables, coarse sand
9 Wilfley tables, fine sand
concentrate
concentrate
3 Dorr separators, double
6 Tube mills, 52″×16′
3 Dorr thickeners, 30′×10′
30 Johnston's slime concentrators
Solution, to stamp battery
concentrate
Pumps
3 Dorr thickeners, 30′×10′
Solution, to stamp battery
6 Brown agitators, 45′×15′
2 Cyanippus decantors, 45′×15′
Dehne clarifiers
5 Merrill slime presses
Residue, to waste
Precipitating plant (by zinc dust)
3 Merrill precipitation presses
3 Tilting furnaces
Bullion

the same time silver sulphate is produced. Finally at a bright red heat (1085°, according to Friedrich) silver sulphate is split up and metallic silver remains with the oxides of iron and copper. The action is carefully watched and the operation stopped when the copper sulphate has been almost all decomposed, and the silver sulphate is at its maximum. The roasted matte is then extracted with hot water, and the silver precipitated by means of metallic copper. The process requires skill and care, and the losses of silver are by no means insignificant.

In another group of processes the silver in sulphide ores is roasted with salt with the production of silver chloride, which is dissolved by a hot solution of common salt (*Augustin process*), by sodium thiosulphate (*von Patera process*), or by calcium thiosulphate (*Kiso process*). In the *Russell process* a solution of sodium-copper thiosulphate ('extra-solution') is used after the ordinary thiosulphate has been drawn off. In this way some metallic silver and undecomposed silver sulphide is extracted as well as the silver chloride. Precipitation is effected by metallic copper in the Augustin process, and by a soluble sulphide when a thiosulphate is used as the solvent for silver. These processes are now obsolete, being generally less advantageous than cyaniding.

SMELTING SILVER ORES.

Argentiferous lead and copper ores are smelted for lead and copper respectively, the silver being concentrated in the resulting pigs of metal or in mattes, speiss, or other intermediate products. In making up the charges for the blast furnaces in lead smelting, poor sulphide ores are first roasted and all silver ores, even if they contain no lead, may be mixed with the lead ore and their silver extracted. In each case consideration is paid to the composition of the silver ore and to the possibility of treating it more profitably in other ways. The lead usually amounts to 10 or 12 p.c. of the charge, and the coke to from 7·5 to 16 p.c. Blast furnaces of moderate size are used and argentiferous lead, some matte, and a fusible slag consisting chiefly of silicates of lime and iron with various impurities are produced. For the details of smelting, *see* LEAD and COPPER.

The pig lead or 'base bullion' contains varying quantities of silver up to about 2 p.c. It is not usual to allow this proportion to be exceeded, on account of loss in the slag. The distribution of silver in the lead is irregular and it is difficult to obtain trustworthy samples for assay. The most satisfactory method is to melt the lead and to dip out a small part as a sample.

The *desilverisation of lead* is effected by the Pattinson process, now almost obsolete, by the Rozan process, or by Parke's process, followed in each case by cupellation. In the Pattinson process a charge of 10 or 15 tons of molten lead contained in an iron pan is allowed to cool, and the crystals of nearly pure lead first formed are separated from the mother liquor, which contains practically all the silver. In the original Pattinson process the crystals were removed by perforated ladles and the operation continued until the enriched lead contained about 1 p.c. of silver. The limit of richness would be reached when the lead contained 2·5 p.c. of silver, the composition of the eutectic alloy. In a later modification of the process the charge is kept stirred by revolving paddles or by jets of steam (Rozan process) and the mother liquor drawn off by tapping, after about two-thirds of the lead has been converted into crystals. The operation is repeated until the rich lead contains about 2 p.c. of silver, and the poor lead from 0·001 to 0·003 p.c.

Parke's process depends on the fact that if molten zinc is stirred into a bath of argentiferous lead, which is afterwards allowed to cool somewhat, the zinc extracts the silver from the lead, and rises to the top forming a crust, which contains the silver and any gold or copper that may be present. The total amount of zinc added is usually about 1½ or 2 p.c. of the weight of the lead, but it is not all added at once. Two or three successive additions are made, and the crusts removed by perforated ladles as soon as they begin to form. The first crust contains almost all the gold and copper. Only about 0·0005 p.c. of silver is finally left in the lead, which also retains 0·6 p.c. of zinc.

The zinc crusts contain much lead which is in part separated by liquation, the crust being heated to the melting-point of lead, when some of the lead flows away. After liquation the rich scums are usually treated by retorting, the zinc being distilled and recovered for further use. Faber du Four tilting furnaces (Fig. 5), each containing a single large pear-shaped graphite retort, are in wide use. These furnaces take a charge of 8–10 cwts. of rich scums. After distillation the residue consists chiefly of lead and silver, containing from 5 to 10 p.c. of the latter. It is treated by cupellation.

Another method of treating the rich scums is to oxidise the zinc with steam and dissolve it in sulphuric acid. This method can be used only if there is a ready market for the zinc sulphate. In the Schnabel process the zinc oxide is dissolved out by ammonium carbonate. For further details concerning the desilverisation of lead, *see* LEAD.

The electrolytic method used in the desilverisation of copper has already been described under COPPER.

Cupellation consists in melting argentiferous lead in a reverberatory furnace and oxidising it by means of a blast of air which is directed upon its surface. The litharge flows to the edge of the molten bath of metal, carrying with it the oxides of other base metals, and is drawn off through narrow channels in the hearth. When all the lead has been oxidised the silver remains in the furnace in a partially refined state. The hearth of the furnace consists of marl, boneash, Portland cement and crushed firebrick, or magnesia, materials which resist the corrosive action of molten litharge. The temperature is kept above the melting-point of litharge, which is from 825° to 900°, as pasty litharge is likely to carry away considerable quantities of entangled silver.

The litharge formed at the beginning of cupellation contains the greater part of the readily oxidisable impurities such as iron, zinc, and tin. Arsenic and antimony are oxidised more slowly, and copper, bismuth, and tellurium are retained by the metal bath until most of the lead has been removed. Molten litharge absorbs oxygen from the air, and gives it up again to copper, bismuth, &c., which are in great part oxidised in that way. Silver is lost by volatilisation and also by being carried away in the litharge, probably as oxide in the first place. The total loss of silver is usually not more than 0·5 p.c. Cupelled silver may be 998 fine, containing only 2 parts of impurities per 1000, but is often impure, requiring to be cupelled again with fresh lead.

The separation of litharge from the metal-bath is due to its lower density and lower surface tension. Anything that lowers the surface tension of the metal-bath increases the loss of silver (Smith, Trans. I.M.M. 1908, 17, 463).

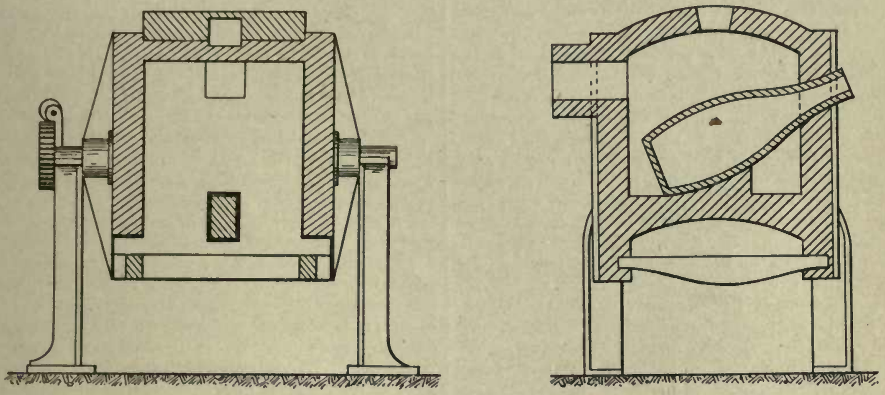


FIG. 5.

There are two types of furnace, the German and the English cupellation furnaces. The German furnace takes a charge of from 5 to 30 tons of argentiferous lead. It has a fixed hearth forming part of the furnace and a movable top or hood which is lifted off by a crane, when the work is at an end, to facilitate cooling, the removal of the silver, &c. The charge is melted very slowly so as to eliminate certain mechanically mixed impurities, especially sulphides and copper, which form a dark scum (*Abzug*) on the surface of the molten metal, and are raked off before the blast is turned on. Then *Abstrich*, consisting chiefly of arseniates and antimoniates, is formed and raked off, after which pure litharge (*glätte*) is formed and allowed to flow away. The litharge is often sold as such, without further treatment. Towards the end of the operation the litharge becomes more and more contaminated with copper, bismuth, &c. The final result, in one method of working, is an impure silver (*Blicksilber*) containing 5–10 p.c. of impurities. The silver is allowed to solidify and the cake is cooled with water, broken into pieces while still hot, and refined by a second cupellation (*Feinbrennen*) with fresh lead in a special furnace or by treatment in pots. The fine silver is cast into bars.

The English cupellation furnace has a fixed hood, but the hearth or test is removable from the furnace. It is much smaller than the German furnace, containing from half a ton to five tons of work-lead. It is used for richer silver-lead alloys than the German furnace. The litharge produced usually contains too much silver for it to be sold without further treatment. The silver-lead is usually enriched until it contains 50–70 p.c. of silver, when it is ladled out into moulds and a fresh charge added to the furnace. The test eventually wears thin, when it is withdrawn and another test substituted. Rich silver-lead is cupelled to pure silver in a separate furnace at a higher temperature than before, and is then ladled out into moulds.

In Fig. 6 an American type of English cupellation furnace is shown, described by Hofman (Metallurgy of Lead, 5th ed. 519). The plan is on the section *xx* in the elevation. Here *a* is the fireplace, *b* the test, and *c* the flue. The space underneath the test is hollow. In this furnace the test is 4 ft. 4 in. by 3 ft. 6 in., and the old oval shape has been modified. For further details of cupellation, *see* LEAD.

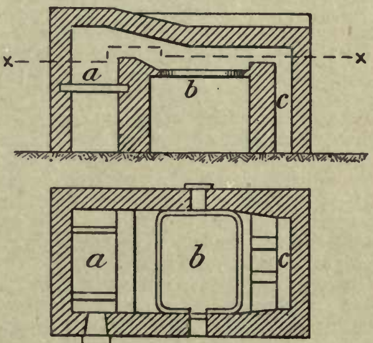


FIG. 6.

Refining. Silver bullion produced by the methods already described usually contains gold as well as impurities such as copper, iron, lead, zinc, &c. For the methods of parting it from gold, *see* GOLD. In these processes the base metals are also separated. Doré silver containing only a few parts of gold per 1000 is either treated alone or melted with crude gold bullion with the formation of a parting alloy.

The anode mud formed in the treatment of argentiferous copper by electrolysis (*see* Copper) may contain a high percentage of silver. For example, a sample of anode slimes from converter copper at Anaconda was found by Keller (J. Amer. Chem. Soc. 1897, 19, 10; Min. Indus. 1898, 239) to contain 55·15 p.c. of silver and 0·20 p.c. of gold, together with 13·82 p.c. of copper, 10·68 p.c. SO_4, and 8·35 p.c. of Pb, Bi, Sb, As, Te, Se, and Fe. Such material was formerly treated by boiling with sulphuric acid and precipitating the silver by copper. Various modifications of this process have been introduced such as the Cabell-Whitehead process of boiling with silver sulphate and dilute sulphuric acid, by which the copper was obtained in solution and the silver in the residue. Lead, arsenic, &c., may be removed by melting in a reverberatory furnace, or, if present in small quantities only, by treatment in crucibles. The Moebius process of electrolysis is described under Gold.

Silver obtained by amalgamation, by the lixiviation processes, or in the form of 'Blicksilber' by cupellation is often refined in crucibles. In Rössler's process (Schnabel and Louis' Metallurgy, vol. i. 729) silver sulphate is added to the metal to eliminate lead, bismuth, and more oxidisable metals. The silver is melted in plumbago crucibles and covered with a layer of sand. The silver sulphate is then added and stirred in with an iron rod. It is decomposed (at 1085°, according to Friedrich) into silver, sulphur dioxide, and oxygen, and the base metals are oxidised by the latter. At Lautenthal three or four successive additions of silver sulphate are made in treating 'Blicksilber' which is 950–980 fine, the total amount of silver sulphate added being from 1½ times to twice the weight of the impurities. The slag consists of silicates of iron, lead, bismuth, &c., and contains 1·88 p.c. of silver according to an analysis by Hampe.

Another method of refining such silver is to pass air through the molten metal contained in pots and covered by a layer of sand (Rose, Trans. I.M.M. 1905, 14, 377).

Cement silver which contains silver chloride is melted with caustic potash or soda. Thus at Schmöllnitz (Schnabel and Louis, *l.c.*) 246 lbs. of cement silver are melted in a plumbago crucible with 1–5½ lbs. of caustic potash in order to decompose the silver chloride and 5–20 oz. of saltpetre for the oxidation of antimony, &c. The process lasts about 6 hours.

Uses of silver. Silver is mainly used in the form of its alloys with copper for conversion into coin, plate, and jewellery. The alloys used in coinage contain from 400–945 parts of silver per 1000, the most usual standards being 835, 900, and 925 (*see* Rose's 'Precious Metals,' 239). For details of coinage, *see* Gold. Silver wares are of many different standards (*see* 'Precious Metals,' 245).

Silver plate often contains 0·5 p.c. of cadmium to facilitate the production of sound malleable castings. The ingots of silver are rolled out into sheets, which are pickled and slit into strips for the production of wire, or stamped out and the pieces shaped by striking between dies. Silver-plating is carried out in cyanide baths containing about 3 oz. of potassium cyanide and 1 oz. of silver per gallon of water.

Production of silver. The annual production of silver has risen almost continuously since 1830. In 1830 the world's production was about 460,000 kilogs., in 1880 2,500,000 kilogs., in 1900 5,600,000 kilogs., and in 1910 7,267,463 kilogs., valued at £24,563,000. The production depends largely on that of lead and copper by smelting, in which silver is a bye-product.

The largest amount of silver is produced by Mexico, followed by the United States and Canada. These three countries between them account for about 70 p.c. of the world's product. The price of silver is quoted in London in pence per standard oz., 925 fine, and in the United States in cents per fine ounce. It was about 60 pence per standard ounce from 1830 to 1873, but afterwards it fell almost continuously with some fluctuations until 1902, when it was 24 pence. The price in 1912 was about 28 pence per standard ounce.

Alloys of Silver. The *silver-copper* alloys are by far the most important of these commercially. The addition of a few per cent. of copper to silver lowers its melting-point, prevents it from effervescing on solidification, enables sound castings to be made, and makes it harder without sensibly impairing its malleability or altering its colour. The superiority of such alloys over pure silver, as well as their lower cost, led to their use in coinage and for ornaments in very early times. For the melting-points of the alloys, *see* Heycock and Neville (Phil. Trans. 1897, 189 A. 25). Levol's alloy, containing 71·89 p.c. of silver, is the alloy of lowest melting-point (eutectic alloy), solidifying at 778°. This alloy is uniform in composition, but in the others segregation takes place on solidification, those containing more than 71·89 p.c. of silver, becoming richer in silver in the interior than on the outside, and those with less than 71·89 p.c. of silver changing in the reverse direction. The difference in composition, however, between the inside and the outside of an ingot never exceeds a few parts per thousand. For the specific gravity of the alloys, *see* Karmarsch (Dingl. poly. J. 1877, 226, 335). The density of British silver coin and plate (925 fine) is 10·37, and that of the 900 standard is 10·31. Various standards, down to 400 fine (*i.e.* silver 40 p.c., copper 60 p.c.), are in use for coinage abroad. The silver-copper alloys blacken when heated in air, but the black oxide of copper is removed and a frosted surface of pure silver produced by treatment with dilute sulphuric acid.

Silver and *lead* mix together in all proportions when molten, but on solidification they separate completely and the alloys undergo segregation, so that they are not uniform in composition. The valuation of argentiferous lead produced in smelting is therefore difficult. The eutectic alloy contains 2·5 p.c. of silver and solidifies at 303°. This freezing-point is observable even in an alloy containing over 99 p.c. of silver (Petrenko, Zeitsch. anorg. Chem. 1907, 53, 200). In alloys containing less than 2·5 p.c. of silver, crystals of nearly pure lead separate out between 326° and 303°. The Pattinson process of desilverisation of lead is based on these properties.

Silver-bismuth alloys are similar to the silver-lead alloys. The eutectic contains 2·5 p.c. of silver and solidifies at 262°. It persists almost to the pure silver end of the series, making all the alloys brittle, particularly if copper is present also. In the latter case annealing is useless, so that a trace of bismuth makes standard silver unfit for coinage.

Silver-mercury alloys. *See* AMALGAMS.

Silver-gold alloys. *See* GOLD.

Silver-zinc alloys are readily formed, zinc removing silver from molten silver-lead alloys. It is probable that in this case the compound $AgZn_{12}$ is formed, which melts at about 430°, and rises to the top of the lead-bath forming a crust in which some lead is entangled. The zinc can be removed from the alloy by distillation or treatment with acid.

Alloys of silver with tin, platinum, aluminium, thallium, and nickel have also been studied.

Bibliography. Detailed information on the metallurgy of silver may be found in Percy's Silver and Gold, 1880, H. F. Collins' Metallurgy of Lead and Silver, 1900, Schnabel and Louis' Handbook of Metallurgy, 1907, Rose's Precious Metals, 1909; in the transactions of various societies such as the Institution of Mining and Metallurgy, London, the American Institution of Mining Engineers, and the Chemical, Metallurgical, and Mining Society of South Africa. *See* also the (annual) Mineral Industry, the (monthly) Mining Magazine and the weekly journals, the Mining Journal, the Mining and Scientific Press (San Francisco), the Engineering and Mining Journal (New York), and the Mexican Mining Journal. T. K. R.

Colloidal silver was first obtained by Carey Lea (Amer. J. Sci. 1889, 37, 476; *ibid.* 38, 47, 129; *ibid.* 1894, 48, 343; Phil. Mag. 1891, 31, 238, 320, 497; 32, 337) by the reduction of silver salts with the metallic salts of organic and inorganic acids. Dextrin or tannin may also be used as reducing agents. Colloidal silver is prepared by adding to 500 c.c. of a 10 p.c. silver nitrate solution, a mixture of 280 grms. of crystallised sodium citrate dissolved in 500 c.c. of water and 500 c.c. of a 30 p.c. solution of crystallised ferrous sulphate with constant stirring. The precipitate is washed by decantation with dilute sodium citrate solution, dissolved in water and reprecipitated by the addition of absolute alcohol. As thus prepared it is a pale lilac, blue or green-coloured mass forming a deep-red aqueous solution.

Colloidal silver may be prepared by passing an electric current between silver poles under water. With a small current brown solutions of low conductivity are obtained, whereas with stronger currents, the particles of silver increase in size and the solutions become greenish or bright green, and possess a greater conductivity. The conductivity of colloidal silver solutions, which is greater than that of water, is supposed to be due to the presence of silver oxide (Rebière, Compt. rend. 1909, 148, 354). The addition of an electrolyte also converts the brown into a green solution (*see* also Woudstra, Zeitsch. physikal. Chem. 1908, 61, 607; Lottermoser, *ibid.* 62, 284).

Solutions of colloidal silver are also said to be obtained by heating silver with distilled water for a long time (Traube-Mengarini and Scala, Atti. R. Accad. Lincei, 1909, [v.] 18, 542).

Colloidal silver may also be obtained by heating silver nitrate with an alkaline solution of proto- or lys-albinate (Paal, Ber. 1902, 35, 2206), or with formaldehyde and sodium silicate (Küspert, *ibid.* 1902, 35, 2815, 4066, 4070), or with acraldehyde and gelatin solution (Castoro, Gazz. chim. ital. 1907, 37, i. 391). In the last case the solutions have the colour of bromine and may be kept for years without changing their colour and properties.

According to an U.S. Pat. (701606, 1902) a colloidal silver, distinguished by its property of retaining its solubility in dilute alkalis after having been precipitated from aqueous solutions by acids, is obtained by the action of silver chloride on an alkaline solution of the products of decomposition of albumins by warm dilute alkalis (J. Soc. Chem. Ind. 1902, 916).

For other methods of preparing colloidal silver, *see* Schneider (Ber. 1891, 24, 3370; 1892, 25, 1164, 1281, 1440); Barus and Schneider (Zeitsch. physikal. Chem. 1891, 8, 278; Wied. Ann. 1893, 48, 357); Oberbeck (*ibid.* 745); Blake (Amer. J. Sci. 1903, 16, 282); Lottermoser and Meyer (J. pr. Chem. 1897, 56, 241; *ibid.* 1898, 57, 540); Lottermoser (*ibid.* 1905, 71, 296); Chassevant (Bull. Soc. chim. 1904, 31, 11); Gutbier and Hofmeier (Zeitsch. anorg. Chem. 1905, 45, 77); Kohlschütter (Zeitsch. Elektrochem. 1908, 14, 49).

The colour of colloidal silver varies very largely with the mode of preparation; it has never been obtained absolutely pure and, according to Hanriot (Compt. rend. 1903, 137, 122), the different varieties are distinct chemical individuals, the 'impurity' forming an integral part of the molecule. Their colour is affected by light, but this change is said to be prevented by the addition of certain organic liquids (Gallagher, J. Phys. Chem. 1906, 10, 701). All forms of the solid are brittle, easily powdered, amalgamate with mercury, and are instantly converted by acids into normal grey silver, without evolution of gas.

Colloidal silver is sometimes known as *collargol* in therapeutics, but this name (according to Hanriot, *l.c.*) should only be applied to those forms which contain albuminoid matter, or a certain characteristic grouping (Danlos and Cothereau, J. Soc. Chem. Ind. 1903, 315, 514; Hanriot, Compt. rend. 1903, 136, 680, 1448).

Colloidal silver is used in medicine, chiefly for the preparation of Credé's ointment (*Unguentum Credé*), which is composed of 15 parts colloidal silver, 5 of water, 10 of white wax, and 70 of benzoinated lard. The ointment is used in the treatment of various forms of septic infection.

Preparations containing colloidal silver or silver oxide are prepared by treating aqueous solutions of silver salts with an alkaline solution of a tannin (*e.g.* catechu, catechin, kino, &c.), which yield protocatechuic acid and phloroglucinol when fused with potassium hydroxide. The colloidal solutions so formed are freed from alkali and salts by dialysis and then evaporated to dryness in a vacuum. The products are soluble in water and possess the antiseptic properties of colloidal silver and the astringent properties of tannin substances (D. R. P. 208189).

Silver Oxides and Salts.

Silver oxide Ag_2O is obtained as a brown, hydrated precipitate by addition of potash to silver nitrate, or as a bluish-black powder by boiling the precipitated chloride with concentrated potash. It is also formed in small quantities when silver is heated in air or oxygen at 500°–550° (Berthelot, Compt. rend. 1900, 131, 1159).

When dried at 60°–80° it becomes almost black. At ordinary temperature it is soluble in 15,360 parts of water (Levi, Gazz. chim. ital. 1901, 31, ii. 1), the solution having an alkaline reaction and a metallic taste. Acids dissolve it, with production of salts, which are generally anhydrous. The recently precipitated moist oxide absorbs carbon dioxide from the air (Rose, Pogg. Ann. 85, 304). Hydrogen reduces silver oxide to metal at 100°. Tin and copper also reduce it in presence of water, and carbon monoxide reduces it in the dry state at ordinary temperature (Dejust, Compt. rend. 1905, 140, 1250). When heated at 250° it begins to decompose, and above 270° it rapidly loses its oxygen, which is entirely evolved at about 300°–340°.

Silver oxide decomposes soluble chlorides with formation of silver chloride and precipitates the corresponding oxide from solutions of many metallic salts. When rubbed in a mortar with sulphur, phosphorus, antimony, or arsenic sulphides, or with any other readily oxidisable substance, ignition takes place. Silver oxide dissolves in ammonia, but care should be taken in working with ammoniacal silver solutions as dangerous explosions may sometimes occur (Matignon, Bull. Soc. chim. 1908, [iv.] 3, 618; Sieverts, Zeitsch. angew. Chem. 1909, 22, 6).

Silver oxide is used to impart a yellow colour to glass, one process being to dip the warm glass in a flux composed of 20–30 parts of sodium metaphosphate and 4 of silver nitrate, or in the case of small articles, a mixture of clay and silver oxide is applied to the surface and the article heated in a muffle. To obtain a metallic lustre, small quantities of silver nitrate are fused with the material for making glass, and while the melt is still hot the surface is reduced by being exposed to alcohol vapours (Zsigmondy, Dingl. poly. J. 1897, 306, 91, 68). It sometimes replaces the nitrate in medicine, as its discolouring action on the skin after prolonged internal use is much less; on the other hand, its slight solubility causes it to be of perhaps less benefit than the nitrate (Nat. Standard Dispensatory, 1905).

Colloidal silver oxide or hydroxide is said to be contained in an alkaline solution of silver protalbinate and lysalbinate (Paal, Ber. 1902, 35, 2206).

According to Bruce (Chem. News, 1884, 50, 208), the hydroxide $Ag_2(OH)_2$, obtained by mixing dilute solutions of silver nitrate and potash in alcohol of 90 p.c. at −50°F., is almost white. It, however, soon darkens, and is brownish even at −40°F. (*see* also Fr. Pats. 342865, 346066; Carnelly and Walker, Chem. Soc. Trans. 1888, 79; Lohnstein, Chem. Zentr. 1909, ii. 1533). It behaves as a very weak base.

Silver oxide corresponds to the only well-defined series of silver salts, most of which are insoluble in water. The soluble salts have a neutral reaction and an unpleasant metallic taste, and are often poisonous (Chem. Zentr. 1908, i. 56; Izar, Biochem. Zeitsch. 1909, 20, 249, 266).

The silver salts are readily reduced by aldehydes, aromatic amines, and many other organic compounds (Morgan and Mickelthwaite, J. Soc. Chem. Ind. 1902, 1373). Their general stability is said to be increased by the addition of a thickening medium, such as gelatin (Fr. Pat. 321830, 1902).

Silver salts have been suggested for use in the sterilisation of drinking water; the pathological organisms of cholera, typhoid, and dysentery, are instantly destroyed by very small proportions of the disinfectant (Traetta-Mosca, Gazz. chim. ital. 1909, 39, i. 69).

Silver peroxide. The body to which this name is usually applied was first obtained by Ritter in 1804 by the electrolysis of a silver nitrate solution (Berthelot, Compt. rend. 1880, 90, 653; *ibid.* 1901, 132, 897; *ibid.* 1901, 133, 555).

It was for a long time considered to have the composition Ag_2O_2 (Wallquist, J. pr. Chem. [i.] 31, 179; Fischer, *ibid.* 32, 108), but more recent analyses have shown that it contains nitrogen, and has the composition Ag_7NO_{11} or

$$3Ag_2O_2AgNO_3,2O.$$

It is therefore termed *silver peroxynitrate* (Mulder and Heringa, Rec. trav. chim. 1896, 15, 1, 235; Mulder, *ibid.* 16, 57; *ibid.* 1903, 22, 235, 405; Sulc, Zeitsch. anorg. Chem. 1896, 12, 89, 180; *ibid.* 1900, 24, 305; Watson, Chem. Soc. Trans. 1906, 578; Barbieri, Atti. R. Accad. Lincei. 1907, [v.] 16, ii. 72).

According to Baborovský and Kužma (Zeitsch. physikal. Chem. 1909, 67, 48), the silver peroxynitrate consists of the peroxide Ag_3O_4, mixed with silver nitrate (Bose, *ibid.* 1909, 68, 383). Similar peroxy salts are obtained by the electrolysis of other silver salts (Mulder, Rec. trav. chim. 1900, 19, 115; Tanatar, Zeitsch. anorg. Chem. 1901, 28, 331).

When silver peroxynitrate is treated with water it reacts thus,

$$Ag_7NO_{11}=AgNO_3+3Ag_2O_2+O_2.$$

The silver nitrate goes into solution, and the peroxide thus obtained (Watson, *l.c.*) is precipitated as a greyish-black powder, sp.gr. 7·44 (approximately), which may be heated to 100° without change. At a higher temperature it evolves oxygen and deposits silver. With ammonia it reacts thus

$$6Ag_2O_2+2NH_3=N_2+3H_2O+3Ag_4O_3,$$

the latter oxide has, however, not been isolated (*see* also Berthelot, *l.c.*).

Both the peroxy salts and the peroxide dissolve in cold, strong nitric acid, forming an intensely brown solution, and in strong sulphuric acid with an olive-green colour.

Silver peroxide is also said to be obtained by the action of potassium persulphate solution on silver nitrate or silver sulphate (Marshall, Chem. Soc. Trans. 1891, 771), and by the action of ozone on silver. Possibly the oxide Ag_2O_3 also exists (Luther and Pokorny, Zeitsch. anorg. Chem. 1908, 57, 290).

Silver carbonate Ag_2CO_3 is obtained by precipitating silver nitrate with an alkaline carbonate, as a white precipitate, which turns yellow on washing, and is blackened by light. It is said to lose the whole of its carbon dioxide at 200° (Colson, Compt. rend. 1905, 140, 865). A solution of the salt in ammonia gives, on addition of alcohol, a grey precipitate having the composition $Ag_2CO_3,4NH_3$.

According to G. S. Johnson (Chem. News, 1886, 54, 75), it is obtained in crystals by dissolving the precipitated carbonate in water saturated with carbon dioxide at 15°. He has also obtained it in large glistening yellow prisms, which melt at low redness and decompose at a somewhat higher temperature with evolution of carbon dioxide, by exposure of the oxide in presence of water to the air for 2 months. Schulten (Compt. rend. 1887, 105, 881) has obtained a white precipitate which changes to microscopic crystals of the composition $AgKCO_3$, by the addition of silver nitrate to a concentrated solution of potassium carbonate containing free carbon dioxide. Water decomposes the crystals, with formation of the normal carbonate (Reynolds, Chem. Soc. Trans. 1898, 265).

Colloidal silver carbonate can be obtained by adding silver nitrate to sodium proto- or lysalbinate and dissolving the silver-albinate so obtained in sodium carbonate and dialysing the solution (D. R. P. 175794). This can be employed as a general method for the preparation of colloidal silver compounds, such as the phosphate, sulphide and the halides (Paal and Voss, Ber. 1904, 37, 3862).

Silver nitrate $AgNO_3$ is usually prepared by dissolving silver in nitric acid, and is largely so obtained in the 'parting' of silver from gold by nitric acid. The salt may be freed from copper by boiling with freshly precipitated silver oxide, which precipitates the copper as oxide, or by heating the fused salt until the copper nitrate has been decomposed, which occurs before the silver salt is affected. When a portion dissolved in water and treated with ammonia gives no blue colour, the mass is cooled, dissolved in water, filtered from the copper oxide, and recrystallised. In working up photographic and other silver residues, the chloride produced from solutions by addition of hydrochloric acid, and the ash of papers, &c., is mixed with 4 or 5 times its weight of sodium carbonate or of a mixture of potassium and sodium carbonates, and is heated in a crucible to bright redness, when the silver collects as a button in the bottom of the crucible. The precipitated chloride may also be reduced by zinc or iron in water slightly acidulated with hydrochloric or sulphuric acid.

Silver nitrate crystallises in colourless rhombic tables of sp.gr. 4·328 (Schröder, Pogg. Ann. 106, 226), melting at 218° (Carnelley, Chem. Soc. Trans. 1878, 276), and resolidifying to a fibrous crystalline mass. According to Guinchant it melts at 209° (Compt. rend. 1909, 149, 569). At 159° it passes from the monoclinic to the orthorhombic form. When the fused salt is cast in sticks, it forms the *lunar caustic* of pharmacy (Warden, Pharm. J. 1897, 58, 61). At a heat much below redness it is decomposed into silver nitrate, with evolution of oxygen, and at a red heat into silver, nitrogen peroxide, oxygen, and nitrogen. According to Colson it commences to decompose at 350° (Compt. rend. 1909, 148, 837; Divers, Chem. Soc. Trans. 1899, 83).

Water dissolves the nitrate with formation of a neutral solution; hot alcohol dissolves about a fourth of its weight; strong nitric acid has but little solvent action. According to Kremers (Pogg. Ann. 92, 497) its solubility in 100 parts of water is :—

0°	19·5°	54°	85°	110°
121·9	227·3	500	714	1111

(*see* also Landolt Börnstein, Tabellen, 1905, 520).

Tilden and Shenstone (Phil. Trans. 175, 33) find that 100 parts of water at 125° dissolve 1622·5 parts, and at 133° no less than 1941·4 parts of the salt.

Dry silver nitrate absorbs ammonia, with evolution of sufficient heat to fuse it, and production of a compound of the formula $AgNO_3,3NH_3$ (Rose, Pogg. Ann. 20, 153). Ammonia nitrates of the composition $AgNO_3,NH_3$ (Reychler, Ber. 16, 992, and 2421) and $AgNO_3,2NH_3$ (Mitscherlich, Pogg. Ann. 9, 413; and Marignac, Ann. Min. [v.] 15, 25), have also been prepared.

Silver ammonio-nitrate $Ag(NH_3)_2NO_3$ is obtained in white acicular crystals by treating a strong aqueous solution of 5 grms. silver nitrate in 4–5 c.c. of water with a concentrated solution of ammonia until the precipitate first formed is almost redissolved and a faintly opalescent liquid is obtained. This is filtered and 120 c.c. of alcohol is added when the crystals separate out. If ether is used instead of alcohol the salt is obtained in the amorphous state (Castoro, Gazz. chim. ital. 1907, 37, i. 310; Lüppo Cramer, Chem. Zeit. 1904, 28, Rep. 296).

Double nitrates of the composition $AgNO_3,KNO_3$; $AgNO_3,RbNO_3$; and $AgNO_3,NH_4NO_3$ have been obtained by Ditte (Compt. rend. 1885, 101, 878; *see* also Rose, *l.c.*).

Silver nitrate forms fairly stable salts with asparagine, carbamide, urethane, leucine, and other amino derivatives (Castoro, *l.c.*).

It also forms other additive organic compounds (Scholl and Steinkop, Ber. 1906, 39, 4393).

With iodine silver nitrate reacts thus

$$5AgNO_3+3I_2+3H_2O=5AgI+5HNO_3+HIO_3$$

(Pawloff and Schein, J. Russ. Phys. Chem. Soc. 1907, 39, 943).

Senderens (Compt. rend. 1887, 104, 175, and 504) has examined the action of zinc, lead, tin, and aluminium, and of selenium, tellurium, arsenic, phosphorus, iodine, and bromine on aqueous silver nitrate.

Silver nitrate is used as a marking-ink and as a constituent of certain hair dyes, and is very largely employed in photography. It is used in medicine both externally and internally (*v.* Squire's Companion to the British Pharmacopœia, 1890, 79, and the U.S. Dispensatory, 1879, 1088; Nat. Stand. Dispensatory by Hare Caspari, &c., 1905; Pigorini, Atti. R. Accad. Lincei. 1907, v. 16, i. 359). It is also used in chemical analytical work.

An unstable *pernitrate* $AgNO_4$ has been obtained by Baborovský and Kužma Zeitsch. Elektrochem. 1908, 14, 196).

Silver nitrite $AgNO_2$ is best obtained by precipitating silver nitrate solution with potassium nitrite (V. Meyer, Annalen, 1874, 171, 23). It forms a white crystalline powder, difficultly soluble in cold water. From hot solution it separates in yellowish needles or prisms. It does not melt but decomposes freely at 180° (Divers, Chem. Soc. Proc. 1905, 281).

With iodine in carbon tetrachloride it gives a quantitative yield of nitrogen peroxide (Neelmeier, Ber. 1904, 37, 1386).

Triple nitrites with cæsium, lead, strontium, and potassium have been prepared (Jamieson, Amer. Chem. J. 1907, 38, 614), and a double nitrite with cobalt by Cunningham and Perkin (Chem. Soc. Trans. 1909, 1568).

Silver hyponitrite $(AgON)_2$ is a bright yellow salt stable at 100°, but decomposing in air when moist, thus: $2(AgNO)_2=4Ag+N_2+2NO_2$; $4NO_2+(AgNO)_2=2AgNO_3+4NO$ (Divers, J. Soc. Chem. Ind. 1899, 274; Kirschner, Zeitsch. anorg. Chem. 1898, 16, 424).

Silver nitride Ag_3N, or Berthelot's *fulminating silver*, is obtained when freshly precipitated oxide is dissolved in ammonia and the solution exposed to the air (Crell's Annalen, 1788, 2, 390; Raschig, Annalen, 1886, 233, 93).

It forms a black powdery precipitate or black lustrous crystals. When dried, it explodes violently on the slightest friction; in fact, explosion frequently occurs even under water. Acids convert it into ammonia and silver salts.

It is often mixed with metallic silver, and sometimes contains hydrogen, when it corresponds to the formula $NHAg_2$. A yellow nitride of silver is said to be formed by heating together silver nitrate and magnesium nitride in a sealed tube (Smits, Rec. trav. chim. 1896, 15, 135).

Silver amide $AgNH_2$ is formed by adding a solution of potassamide in liquid ammonia to an excess of silver nitrate in the same solvent. It is white, is soluble in liquid ammonia, and in ammonium salt solutions, darkens on exposure to light and explodes readily when dry (Franklin, J. Amer. Chem. Soc. 1903, 25, 827).

Silver azoimide AgN_3 forms minute crystals insoluble in water and very explosive. It is obtained by adding silver nitrate to an azoimide solution.

A molybdenum silver cyanamine

$$[Ag_4NH_3]Mo(CN)_8$$

is described by Rosenheim (Zeitsch. anorg. Chem. 1909, 65, 166).

Silver cyanide $AgCN$ is obtained as a white, curdy precipitate by addition of a soluble cyanide to silver nitrate solution. It dissolves readily in ammonia and soluble cyanides, and when heated with water or caustic potash is reduced to silver (Marsh and Struthers, Chem. Soc. Proc. 1902, 249). Sulphuric, hydrochloric, or boiling nitric acid decomposes it with evolution of hydrocyanic acid (Plimmer, Chem. Soc. Trans. 1904, 12).

The ammoniacal solution contains the compound $AgCN{\cdot}NH_3$, while the cyanide solutions contain double cyanides, such as $AgCN{\cdot}KCN$; $AgCN{\cdot}NaCN$; $3AgCN{\cdot}2KCN{\cdot}NaCN$ (Baup, Ann. Chim. Phys. 1852, [iii.] 53, 462). The double cyanide of silver with a heavy metal is best obtained by addition of silver potassium cyanide to a solution of a salt of the metal. Silver potassium cyanide, which is employed in the electroplating bath (*v.* ELECTROPLATING), crystallises in regular octahedra, soluble in 4 parts of water at 20°, and in 25 parts of alcohol of 85 p.c. at 20° (Baup, *l.c.*; *see* also Bailar, J. Soc. Chem. Ind. 1910, 1085).

Silver cyanate $AgCNO$ is a white, somewhat soluble powder, which explodes on heating. It may be obtained by the addition of silver nitrate to potassium cyanate solution.

Silver thiocyanate $AgSCN$ is a white, curdy precipitate readily soluble in ammonia.

Potassium silver thiocyanate $AgK(SCN)_2$, formed when silver thiocyanate is dissolved in potassium thiocyanate, melts at 140°, and is decomposed by water.

Silver sulphate Ag_2SO_4 may be obtained by dissolving the metal in concentrated sulphuric acid or by dissolving the oxide or carbonate in the acid. It dissolves easily in sulphuric or nitric acid, but requires about 200 parts of cold or 68·58 parts of hot water for solution (Kremers, Pogg. Ann. 92, 499).

Silver sulphate crystallises in small rhombic prisms isomorphous with anhydrous sodium sulphate (Mitscherlich, *ibid.* 12, 138), and fusing at 654° (Carnelley, Chem. Soc. Trans. 1878, 279).

An acid salt $HAgSO_4$ crystallising in pale-yellow prisms, and a double sulphate with aluminium (silver alum)

$$Ag_2SO_4,Al_2(SO_4)_3,24H_2O$$

(Church, Chem. News, 1864, 9, 155) are also known. The latter salt crystallises in octahedra, which are decomposed by water into the component sulphates.

Silver sulphate also forms double salts with tin and antimony sulphates (Weinland and Kühl, Zeitsch. anorg. Chem. 1907, 54, 244, 256).

According to Carey Lea (Amer. J. Sci. 1892, 44, 322) the double salt Ag_4SO_4,Ag_2SO_4,H_2O is produced when silver nitrate is reduced with hypophosphorous acid in presence of sulphuric acid. It forms a pale-brown powder which, however, cannot be wholly purified from phosphoric anhydride.

Silver sulphite Ag_2SO_3 is obtained in small, white glistening needles, or as a white curdy precipitate, by dissolving silver oxide in sulphurous acid and crystallising, or by precipitating a silver salt with sulphurous acid or a sulphite. Several double alkaline sulphites are known.

Silver sulphite and the alkali silver sulphites, when boiled with water or heated at 100°, are converted into dithionates and only after raising the temperature do they decompose, forming sulphur dioxide and silver sulphate (Baubigny, Compt. rend. 1909, 149, 735, 858).

Silver thiosulphate or hyposulphite $Ag_2S_2O_3$ is obtained as a snow-white, slightly soluble powder, of sweetish taste, by addition of dilute silver nitrate to excess of concentrated sodium thiosulphate (*v.* Herschel, Edin. Phil. J. 1819, 1, 26 and 2, 154). It forms double salts with the alkali metals (Richards and Faber, Amer. J. Sci. 21, 167; Rosenheim and Steinhauser, Zeitsch. anorg. Chem. 1900, 25, 72; Gädicke, Zeitsch. angew. Chem. 1903, 16, 608). The salt $NaAgS_2O_3$ is obtained by evaporating a solution of silver chloride in sodium thiosulphate, or better by adding a neutral solution of silver nitrate to a solution of sodium thiosulphate until a permanent precipitate is formed, after which the solution is filtered and alcohol is added. The salt is thus precipitated in silky laminæ.

The ammoniacal solution of this salt may be used for silvering. Cohen (Chem. Soc. Trans. 1887, 39) has described a thiosulphate of the composition $Ag_2S_2O_3,2K_2S_2O_3$.

Silver sulphide Ag_2S occurs native in *argentite, vitreous silver*, or *silver glance*. As double sulphide, it occurs in red silver ore $3Ag_2S,Sb_2S_3$. It may be obtained by heating silver chloride in a current of sulphuretted hydrogen, by heating silver with sulphur or sulphuretted hydrogen, or by precipitating silver solutions with sulphuretted hydrogen.

Silver sulphide melts at 812° when pure (Friedrich, J. Soc. Chem. Ind. 1908, 403). It is sufficiently soft to be cut with a knife, and fuses readily without change, but when roasted in the air becomes gradually converted into silver. It is decomposed by boiling strong sulphuric, nitric, or hydrochloric acid (Gruener, J. Amer. Chem. Soc. 1910, 32, 1030), and is converted into the chloride by digestion with cuprous chloride solution. The presence of sodium chloride facilitates the latter reaction, which is employed for removing silver from certain ores by dissolving the silver chloride as fast as formed.

A mixture of silver sulphide and silver sulphate in molecular proportions forms a viscous dark red-brown fluid at 365°, which imparts to glass immersed in it a dark-brown colour, the shade depending on the time of immersion. The glass so coloured is opaque to blue and ultra violet rays, and may be used for photographic purposes.

Silver sulphide forms double salts with other metallic sulphides.

Silver disulphide Ag_2S_2 is obtained by mixing a solution of silver nitrate in benzonitrile with a solution of sulphur in carbon disulphide. It is a brown amorphous powder insoluble in all ordinary solvents. Heated in a test tube it melts and then decomposes. It is also decomposed by hydrochloric and by nitric acids (Hantzsch, Zeitsch. anorg. Chem. 1899, 19, 104).

Silver sub-sulphide *v. Silver sub-salts*, &c.

Silver selenide Ag_2Se is a dark-grey body, which melts at 834°–850° to a silvery mass (Friedrich and Leroux, Metallurgie, 1908, 5, 355). It is obtained by heating silver with selenium, or by precipitating a silver solution with seleniuretted hydrogen. A di-selenide Ag_2Se_2 is also known. Selenides of silver and lead (*naumannite*) and of silver and copper (*eukarite*) occur in nature; double compounds with antimony and bismuth are described by Pélabon (Compt. rend. 1908, 146, 975).

Silver chromate Ag_2CrO_4 is obtained in dark-red crystals by the addition of potassium chromate solution to silver nitrate. It dissolves in alkaline chromates and in the nitrates of ammonia and the alkalis (R. F. Carpenter, J. Soc. Chem. Ind. 1886, 286; and Biscaro, Chem. News, 1886, 53, 67; Baxter, J. Amer. Chem. Soc. 1909, 31, 529, 541).

When the red salt is dissolved in dilute acetic acid and the solution is concentrated, a greenish-blue modification is formed (Margosches, Zeitsch. anorg. Chem. 1906, 51, 231). By precipitating silver chromate in the presence of albuminous substances, a colloidal form of the salt is obtained (D. R. P. 166154; Chem. Zentr. 1906, i. 617).

By cooling a hot ammoniacal solution of silver chromate yellow crystals of $Ag_2CrO_4,4NH$ are obtained.

Silver thiochromate and double salts of the chromate with phosphoric anhydride and other compounds are known. Possibly potassium silver chromate may exist (Gröger, *ibid.* 1907, ii. 516).

Silver chromate has been employed in miniature painting.

Silver dichromate $Ag_2Cr_2O_7$ is obtained in dark, reddish-brown, triclinic prisms, somewhat soluble in water, by precipitating a boiling solution of silver nitrate, acidified with nitric acid, with potassium dichromate solution (Autenrieth, Ber. 1902, 35, 2057; Mayer, *ibid.* 1903, 36, 1740; Baxter, *l.c.*).

Silver phosphates. Several phosphates are known. The normal *orthophosphate* Ag_3PO_4 is obtained as a lemon-yellow powder, insoluble in water, but readily soluble in acids and ammonia, by precipitating a silver nitrate solution with an orthophosphate. It may be obtained in rhombic dodecahedra (Joly, Compt. rend. 1886, 103, 1071). It fuses at about 849° (Carnelley, Chem. Soc. Trans. 1878, 280). The *diargentic phosphate* Ag_2HPO_4 may be obtained in colourless hexagonal prisms (Joly, *l.c.*), which become yellow in contact with water or alcohol, with decomposition into the normal salt and phosphoric acid. *Silver pyrophosphate* $Ag_4P_2O_7$ is obtained as a white precipitate by addition of sodium pyrophosphate to silver nitrate. It fuses at 585° (Carnelley, *l.c.*) to a brown liquid, which re-solidifies to a white mass of radiating crystals. It is soluble in ammonia, from which it is precipitated unchanged by acids. The *dihydrogen pyrophosphate* $H_2Ag_2P_2O_7$ is formed by heating the pyrophosphate with aqueous phosphoric acid. It is a white powder, m.p. 240° (Cavalier, Compt. rend. 1904, 139, 284). The *metaphosphate* $Ag_2P_2O_6$ or $AgPO_3$ is obtained as a crystalline powder, slightly soluble in water, and fusing at 482° (Carnelley, *l.c.*) to a transparent glass, by precipitating silver nitrate with sodium metaphosphate.

Colloidal silver phosphate is obtained by adding silver nitrite to a solution of sodium phosphate and sodium protalbinate (D. R. P. 175794; Paal and Voss, *l.c.*).

A silver phosphate emulsion for photographic purposes is prepared by adding a large excess of disodium phosphate to a solution of silver nitrate and gelatin. Potassium chlorate, citric acid, and, if necessary, chrome alum are then added (Fr. Pat. 378305, 1907).

A number of silver nitrogen phosphates (Stokes, Amer. Chem. J. 1894, 16, 137; *ibid.* 1896, 18, 646, 658; *ibid.* 1898, 20, 757), and silver thiophosphates (Ferrand, Ann. Chim. Phys. 1899, [vii.] 17, 388; Glatzel, Zeitsch. anorg. Chem. 1893, 4, 215) have been prepared.

Silver phosphites and hypophosphites are also known (Sänger, Annalen, 1885, 232, 14; Gutbier, Zeitsch. anorg. Chem. 1902, 32, 350).

Silver biphosphide AgP_2 is obtained by passing phosphorus vapour over finely divided silver or silver chloride at 400° (Granger, Compt. rend. 1897, 124, 896). A number of other phosphides are described in earlier literature, but it is doubtful whether they exist.

Silver arsenate Ag_3AsO_4 is a dark-red, crystalline powder obtained by the addition of boiling silver nitrate solution to concentrated arsenic acid or to an arsenate. The silver mercury compound $AgHg_2AsO_4$ is described by Jacobsen (Bull. Soc. chim. 1909, [iv.] 5, 947).

Silver arsenite Ag_3AsO_3 is a canary-yellow powder. Its ammoniacal solution when boiled deposits silver. Other arsenates and arsenites, as well as similar compounds with antimony, tellurium, lead, and other metals are known.

Silver plumbite PbO_2Ag_2 is obtained by adding silver nitrate solution made alkaline with potash and to which ammonia has been added, to an excess of lead nitrate. It forms brown crystals, sp.gr. 8·60, which become greyish-black on heating without losing their lustre, form, or general properties; it is insoluble in water, ammonia, or caustic potash, soluble in hot acetic, and fairly so in cold nitric, acid. It yields an olive-green powder and gives a black streak (Bullnheimer, Ber. 1898, 31, 1287).

SILVER AND THE HALOGENS.

Silver chlorides. Two chlorides are said to exist, the normal salt AgCl and the sub-chloride Ag_2Cl (?). Peculiar compounds which appear to be combinations of the normal and sub-chloride, and which are known as photochlorides, are also known. Regarding them and the sub-chloride, and the action of light on silver salts *v. Silver sub-salts*, &c.

The normal silver chloride occurs in *horn silver* or *cerargyrite*, and as the double chloride and bromide of silver in *embolite*. It is obtained by the action of chlorine or hydrogen chloride on silver, or as a dense, curdy, white precipitate, which gradually becomes powdery, by addition of hydrochloric acid or a soluble chloride to silver nitrate solution. Silver chloride assumes a yellow colour when heated, has sp.gr. 5·5, and melts at 460° (Carnelley, Chem. Soc. Trans. 1878, 278; Ramsay and Eumorfopoulos, Phil. Mag. 1896, [v.] 41, 360). It solidifies to a soft, tough, horny mass, having a sp.gr. of 5·594 (Schröder, Pogg. Ann. 106, 226). According to Kohlrausch, the electric conductivity of silver chloride exceeds that of the bromide or iodide, and when fused exceeds that of sulphuric acid. *See* also Böttger (Zeitsch. physikal. Chem. 1906, 56, 83); Le Blanc and Kerschbaum (Zeitsch. Elektrochem. 1910, 16, 242, 680). At a white heat silver chloride volatilises.

The fused chloride is not appreciably soluble in cold water, although very slightly soluble in hot (Stas, Compt. rend. 1871, 73, 710; Böttger, *l.c.*; Drucker, Zeitsch. Chem. Ind. Kolloide, 1909, 4, 216). The precipitated chloride is more soluble, and the washings become cloudy on addition of either hydrochloric acid or silver nitrate. In concentrated hydrochloric acid its solubility is about 1 in 200, and in the acid diluted with its own volume of water 1 in 600. It is much more soluble in alkaline chlorides, especially sodium chloride (Barlow, J. Amer. Chem. Soc. 1906, 28, 1446), and dissolves readily in ammonia. Pure strong nitric acid at 15°–17° dissolves the precipitated chloride to the extent of 2·01 parts in 100,000 (Thorpe, Chem. Soc. Trans. 1872, 453). For the influence of nitric acid on the solubility of silver chloride in mercuric nitrate solution, *see* Buttle and Hewitt (*ibid.* 1908, 1405). Soluble thiosulphates and sulphites, and ferric chloride also dissolve it, and potassium cyanide converts it into a soluble double cyanide AgCN,KCN, together with potassium chloride. It dissolves readily in coniine (Blyth, *ibid.* 1849, 350) and in solution of methylamine (Wurtz, Ann. Chim. Phys. [iii.] 30, 453). Silver chloride is slowly decomposed by boiling concentrated, sulphuric acid (Sauer, Zeitsch. anal. Chem. 1873, 376).

Silver chloride is not reduced by carbon, but may be reduced by fusion with 4 or 5 times its weight of sodium carbonate, or of a mixture of sodium and potassium carbonates. Iron, zinc, and other oxidisable metals reduce it in presence of water, especially when acidified with hydrochloric or sulphuric acid.

Silver chloride is more readily reduced than the bromide (Liesegang, Chem. Zeit. 1901, Rep. 372). It reacts with hydrogen, forming silver and hydrochloric acid (Jouniaux, Compt. rend. 1901, 132, 1270, 1558).

It is also decomposed by intense light (Cordier, Monatsh. 1900, 21, 184; *see* also Baker, Chem. Soc. Trans. 1892, 728; Sonstadt, Chem. Soc. Proc. 1898, 371). Ignited with calcium carbide, metallic silver is deposited (J. Soc. Chem. Ind. 1901, 1020). It also reacts with iodoform giving chloroform and silver iodide (Coninck, Bull. Soc. chim. 1909, [iv.] 5, 62).

Digestion with potassium bromide or iodide solution decomposes the chloride with formation of potassium chloride and silver bromide or iodide (Field, Quart. J. Chem. Soc. 1858, 236). The chloride is converted into the bromide or iodide when fused in a current of air containing bromine or iodine vapour (Julius, Chem. News, 1853, 48, 284). It may be partly converted into the bromide by digestion with bromine water (*v.* Humpidge, Ber. 1884, 17, 1838; Potilizin, J. Russ. Phys. Chem. Soc. 1882, 82, and Ber. 1884, 17, 1308; Berthelot, Compt. rend. 1882, 94, 1619).

Silver chloride, bromide, or iodide, precipitated from solution containing a colouring matter such as an aniline dye, has a characteristic colour which cannot be removed by washing. The compounds produced by the different haloid salts with the same dye frequently differ considerably in colour. Somewhat similar compounds are obtained when silver chloride is precipitated from a solution containing a metallic salt, such as the chloride of iron, cobalt, nickel, manganese, copper, or gold (Carey Lea, J. Amer. Chem. Soc. 34, 384).

Dry precipitated silver chloride rapidly absorbs large volumes of ammonia gas, which it again gives off at 37·7° (Faraday, Quarterly J. of Sc. 5, 74). According to Rose (Pogg. Ann. 20, 157), the amount absorbed corresponds with the formula $2AgCl,3NH_3$.

When a solution of silver chloride in liquid ammonia is allowed to evaporate at −40° to −20°, long colourless needles of the compound $AgCl,3NH_3$ are deposited, but if a solution of silver chloride in concentrated ammonia is evaporated at ordinary temperature, the compound $2AgCl,3NH_3$ separates in colourless prisms (Jarry, Compt. rend. 1897, 124, 288; Ann. Chim. Phys. 1899, [iv.] 17, 327).

Colloidal silver chloride is obtained by the action of chlorine on colloidal silver or by treating the latter with chlorine water until the solution is decolourised, light being excluded during the process. To obtain a precipitate of the soluble chloride, gelatin and ammonium citrate are added (D. R. PP. 103406, 175794; Lottermoser, J. pr. Chem. [ii.] 56, 241; [ii.] 57, 540; *ibid.* 1905, [ii.] 72, 39; Paal and Voss, Ber. 1904, 37, 3862; Ruer, Chem. Zentr. 1905, i. 501; Drucker, Zeitsch. Chem. Ind. Kolloide, 1909, 4, 216).

Silver chloride formed a constituent of the sensitising material used in the original platinotype process (Willis, Photographic J. 1891, 123).

Silver bromide AgBr occurs native as *bromargyrite.* It is obtained by addition of a soluble bromide to silver nitrate, as a yellowish, curdy precipitate, less soluble in ammonia than the chloride, but more so than the iodide. It is also formed by the action of hydrogen bromide, and more slowly of bromine on metallic silver. In dilute ammonia it is almost insoluble. It dissolves in hot hydrobromic acid or mercuric nitrate solution, and crystallises out in octahedra. It is also soluble in potassium and other bromides, forming double salts, and in sodium thiosulphate. According to Vogel (Ber. 1883, 16, 1170; 1885, 18, 861; *v.* also Eder, *ibid.* 18, 1256, and De Pitteurs, Chem. Zentr. 1884, 411), two molecular modifications of silver bromide exist, the one precipitated from aqueous solution, and the other from solution in alcohol of at least 96° p.c. The former is said to be most sensitive to certain of the blue rays, and the latter to certain of the indigo rays.

The solubility of silver bromide in water is found to be 0·107 mgrms. per litre at 21°, and 3·7 mgrms. at 100° (Kohlrausch and Dolezalek, Sitzungsber. K. Akad. Wiss. Berlin, 1901, 1018).

Silver bromide fuses to a reddish liquid at 427° (Carnelley, Chem. Soc. Trans. 1878, 277). Its sp.gr., after fusion, is given by Schröder (Pogg. Ann. 106, 243) as 6·349, that of the precipitated bromide being 6·418. The electric conductivity of silver bromide is less than that of the chloride, but exceeds that of the iodide. When fused it conducts better than sulphuric acid.

Hydrogen chloride decomposes it at 700° with evolution of hydrogen bromide. Chlorine decomposes the freshly precipitated bromide.

According to Rammelsberg (Pogg. Ann. 55, 248), the dry bromide absorbs no ammonia; but it separates from ammoniacal solution in crystals containing ammonia, which is driven off by heat (Liebig, Schweigger's J. 48, 103).

Liquid ammonia below 4° converts silver bromide into a white compound $AgBr,3NH_3$, which loses ammonia at 4°, giving the compound $2AgBr,3NH_3$. The latter loses ammonia at 35°, leaving silver bromide (Jarry, Compt. rend. 1898, 126, 1138).

Colloidal silver bromide is obtained in the same way as the corresponding silver chloride.

Carey Lea describes peculiar compounds produced by precipitating silver bromide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Regarding the sub- and photobromide, and the action of light on silver bromide *v. Silver sub-salts*, &c.

Silver iodide AgI occurs naturally as *iodargyrite* or *iodyrite.* It may be obtained by heating silver with iodine, by dissolving silver in hydriodic acid, or by precipitating silver nitrate with a soluble iodide.

Silver iodide is of a pale primrose colour, and is insoluble in most acids, and almost insoluble in ammonia. Its solubility, however, increases appreciably with a rise in temperature. Its solubility in aqueous ammonia of sp.gr. 0·926 at 16° is 1 in 6000 (Baubigny, Compt. rend. 1908, 146, 263).

Silver iodide absorbs ammonia gas with formation of a white compound, of the composition $2AgI,NH_3$, which evolves ammonia on exposure to the air (Rammelsberg, Pogg. Ann. 48, 170).

It is also readily soluble in liquid ammonia, and when the solution is evaporated at −40° to −10°, a white crystalline compound AgI,NH_3 separates, which at 4° evolves ammonia, forming the compound $2AgI,NH_3$ (Jarry, Ann. Chim. Phys. 1899, [vii.] 17, 327).

Silver iodide dissolves in potassium iodide and soluble thiosulphates; also in hot hydriodic acid, from which it separates on cooling in colourless flaky crystals of the composition AgI,HI (*v.* Deville, Compt. rend. 1851, 32, 894). It is decomposed by hot concentrated nitric or sulphuric acid with evolution of iodine. When gently heated in chlorine, or when heated to 700° in hydrogen chloride, it is converted into the chloride.

When precipitated by excess of potassium iodide, silver iodide is unaffected by light, but it is rendered sensitive by the presence of a trace of silver nitrate, chloride, or bromide, which converts the last trace of potassium iodide into the silver salt (*v.* Abney, Proc. Roy. Soc. 33, 164).

The abnormal expansion and contraction of the iodide when heated was first noticed by Fizeau (Compt. rend. 1867, 64, 304), and has since been examined by Deville (*ibid.* 1867, 64, 323), Mallard and Le Chatelier (*ibid.* 1883, 97, 102), and Bellati and Romanese (Proc. Roy. Soc. 34, 104); and more fully by Rodwell (*ibid.* 33, 97; 25, 280; 31, 291). When heated it acquires a brilliant yellow colour and passes through various shades of orange, until, at 527° (Carnelley, Chem. Soc. Trans. 1878, 278; *see* also Stolzenberg and Huth, Zeitsch. physikal. Chem. 1910, 71, 641), it fuses to an orange-red liquid. On cooling the fused iodide, it contracts considerably at the solidifying-point, and continues to contract, until, at 116°, it expands suddenly and violently, and passes from the amorphous to the crystalline form. The iodide appears to exist in three modifications: (1) as a plastic, tenacious, amorphous, reddish, transparent substance between 116° and its melting-point; (2) as a brittle, opaque, crystalline mass below 116°; (3) as a yellow, brittle, amorphous mass, obtained by pouring the fused iodide into cold water.

The determinations of the specific gravity of the iodide vary considerably. According to Deville (Compt. rend. 1867, 64, 323), the sp.gr. of the fused iodide at 0° is 5·687, that of the precipitated iodide being 5·807 at 0°. According to Kohlrausch the electric conductivity of silver iodide is less than that of the bromide or iodide, but the conductivity of the fused salt exceeds that of sulphuric acid.

A saturated aqueous solution of silver iodide contains 0·0035 mgrms. per litre at 21° (Kohlrausch and Dolezalek, *l.c.*).

Colloidal silver iodide is obtained in the same way as the bromide and chloride, and also by the action of silver nitrate on potassium iodide dissolved in egg albumin (Thum, Amer. J. Pharm. 1910, 82, 507).

Carey Lea has described peculiar compounds produced by precipitating silver iodide in presence of various colouring matters and metallic salts (*v. Silver chlorides*).

Silver iodide, which may be separated from the chloride, with which it is often mixed, by digestion with ammonium carbonate and aqueous ammonia at 70°–80° (Baubigny, Compt. rend. 1908, 146, 335) was formerly employed in medicine, but it is now rarely used.

Regarding silver sub-iodide and photoiodides *v. Silver sub-salts*, &c.

Silver fluoride AgF may be obtained as a deliquescent, very soluble salt, by dissolving silver oxide in hydrofluoric acid. It crystallises from solution in quadratic pyramids, of the composition Ag,FH_2O (Marignac, J. 1856, 129), or in prisms of the composition $AgF,2H_2O$ (Frémy, J. 1856, 87; Pfaundler, J. 1862, 86). The hydrated salt loses water when dried *in vacuô*. Most of the water is driven off, together with some oxygen and hydrofluoric acid, when heated in a covered vessel to the melting-point of lead. After expulsion of all the water, the fluoride may be heated to the melting-point of silver without change. The dry salt absorbs 844 times its volume of ammonia.

When a solution of the fluoride is strongly concentrated over the water-bath, or when the crystallised hydrated fluoride is dried over sulphuric acid, brass-yellow spangles, of the composition $AgF{\cdot}AgHO$, are obtained (Pfaundler, J. 1862, 87; *v.* further, Gore, Phil. Trans. 1869, 191, 192; 1870, 227; 1871, 321).

With aqueous iodoform it reacts thus:

$$3AgF+CHI_3+H_2O=3AgI+HF+CO$$

(Coninck, Bull. Soc. chim. 1909, [iv.] 5, 62).

Silver fluoride has antiseptic properties, and under the name of *tachyol* has been proposed as an efficient and safe disinfectant for drinking waters (Paterno and Gingolani, Gazz. chim. ital. 1907, 37, i. 313).

Silver sub-fluoride *v. Silver sub-salts*, &c.

Silver chlorate $AgClO_3$, formed by passing chlorine through silver oxide suspended in water or by dissolving silver in chloric acid is a white, crystalline substance, m.p. 230°, which when mixed with sulphur detonates violently.

The perchlorate, hypochlorite, and chlorite are also known. Similar bromine compounds, a series of iodates and a number of the silver halogen double salts with the compounds of other metals have been prepared.

Silver iodate is a white crystalline powder, sparingly soluble in water. It is prepared by the action of silver nitrate on potassium iodate, and is employed in medicine externally and internally.

SILVER SUB-SALTS, PHOTOSALTS, AND SUB-OXIDE; ACTION OF LIGHT ON THE HALOID SALTS.

The existence of a suboxide of silver Ag_4O was first affirmed by Wöhler (Annalen, 1839, 30, 1), who stated that when silver citrate is heated to 100° in a current of hydrogen, it is reduced to a sub-citrate and free citric acid, 1 atom of oxygen passing off as water. The residue dissolves in water to a brown solution, from which a black precipitate of the reputed suboxide is deposited on addition of potash. Wöhler's work was repeated by Von Bibra (J. pr. Chem. 1875, [i.] 12, 39), Bailey and Fowler (Chem. Soc. Trans. 1887, 416), Newbury (Amer. Chem. J. 8, 196), and Muthmann (Ber. 1887, 20, 983). According to Bailey and Fowler, carbon dioxide is given off as well as water, except at the very earliest stages of the reduction, and the solution of the resultant body gives the reactions of itaconic acid and shows no argentous citrate. Newbury, however, while also noticing the evolution of carbon dioxide, and failing to obtain a sub-oxide, stated that the red solution is turbid from the presence of finely divided silver, and contains much free citric acid. Bailey and Fowler also failed to confirm Faraday's statement (Ann. Chim. Phys. [ii.] 9, 107), that a sub-oxide Ag_4O_3 is obtained by exposure of a solution of silver oxide in ammonia to the air.

O. v. der Pfordten (Ber. 1887, 20, 1458, 3375) obtained a black compound, which he first described as the suboxide Ag_4O, but to which he subsequently gave the formula Ag_4H_2O (*ibid.* 1888, 21, 2288), by the following process: 20 c.c. of a 12·5 p.c. solution of sodium tartrate was mixed with a solution of 2 grms. of silver nitrate in 1½ litres of water, adding 2 c.c. of a 4 p.c. solution of soda, and stirring vigorously. After 5 hours the liquid was decanted, and the residual black precipitate of argentous tartrate (?) was washed with dilute sodium sulphate and treated with alkali, which converted it into the above compound. The same substance was obtained by the action of alkali on the black precipitate obtained by the gradual addition of 4 c.c. of concentrated phosphorous acid solution to a solution of 10 grms. of silver nitrate in 20 c.c. of water, to which sufficient ammonia had been added to re-dissolve the precipitate at first produced. The body thus obtained is a deep black amorphous powder, which is decomposed by water, and requires to be kept under alkali. It is insoluble in ammonia or acetic acid, and is decomposed, with separation of metal, by hydrochloric, sulphuric, and most other acids, but is not affected in the cold by sulphurous or phosphorous acid. Hydroxylamine has no action in the cold, but reduces it to silver when warmed; mercury fails to remove any silver. When acted on by sulphuretted hydrogen it produces black amorphous sulphide, which becomes grey when dried, and which is slowly decomposed by water. It dissolves in potassium cyanide and in warm dilute nitric and hydrochloric acids, water precipitating it unchanged from the latter. Strong nitric and sulphuric acids decompose it with separation of sulphur.

These results have been disputed by Bailey (Chem. News, 55, 263) and Friedheim (Ber. 1887, 20, 2554; 21, 307), the latter stating that the so-called argentous hydrate is a mixture of silver, with more or less argentic oxide and organic matter. *See* also Lewis (J. Amer. Chem. Soc. 1906, 28, 139). Geuther (Annalen, 114, 121) states that the sub-oxide is obtained by the action of precipitated cuprous oxide on silver nitrate; and, according to Güntz (*see* below), it is obtained by the action of steam on the subfluoride at 160°, but he gives no analysis of the product.

For the preparation of the sub-chloride, to which the formulæ Ag_2Cl (Wöhler) and Ag_4Cl_3 (Von Bibra) have been applied, several methods have been proposed. Wöhler (Annalen, 1839, 30, 3) states that it is obtained as a black powder, which is decomposed by ammonia into silver chloride and silver by the action of hydrochloric acid on argentous citrate prepared as above. Wetzlar (Schweigger's J. 1828, 2, 466) states that it is produced by the action of cuprous or ferrous chloride on silver. Von Bibra (J. pr. Chem. 1875, [i.] 12, 39) and Newbury (*l.c.*) failed to obtain it either by Wöhler's or Wetzlar's process.

Güntz (Compt. rend. 1890, 110, 1337; 1891, 112, 861) prepared a fluoride of the composition Ag_2F by electrolysis of a saturated solution of the normal fluoride with a powerful current, using silver electrodes, and allowing the liquid to become hot. It is thus obtained on the cathode in brass-coloured plates, which are unaffected by dry air, but are rapidly decomposed by water, with precipitation of silver and production of silver fluoride. The same compound is said to be produced when finely-divided silver is heated in a sealed tube, at a temperature below 90°, with silver fluoride solution. Compare Pfaundler (*Silver fluoride*).

According to Güntz the sub-fluoride is converted into the violet *sub-chloride* when dry hydrochloric acid, or, better, the vapour of the chloride of carbon, silicon, or phosphorus, is passed over it. Analysis of the sub-chloride indicates the presence of some normal chloride. Hydrogen iodide similarly gives a *sub-iodide* Ag_2I, with considerable rise of temperature. Sulphuretted hydrogen produces the *sub-sulphide* Ag_4S; and steam passed over the sub-fluoride heated to 160° produces the sub-oxide.

Vogel has prepared the sub-halides according to the following method. Cupric bromide (or other halide) was boiled with copper shavings, and the green solution poured into 10 times the quantity of water and boiled with acetic acid. The white powder so obtained is dried quickly and treated at once with excess of 10 p.c. silver nitrate solution, a blackish-grey *sub-bromide* Ag_4Br_2 is thus obtained, which may be freed from copper by repeated digestion with 20 p.c. silver nitrate solution (J. Soc. Chem. Ind. 1900, 374; Waterhouse, *ibid.* 374).

According to Emszt (Zeitsch. anorg. Chem. 28, 346) Vogel's sub-haloids are not identical with those formed by the action of light on photographic plates.

Carey Lea (Amer. J. Sci. 33, 349, 480, 489; 34, 33) has produced an important series of coloured haloid salts of silver, to which he has given the name 'photosalts,' and which he regards as identical with the so-called sub-salts forming the latent photographic image. They appear to be compounds of the normal and subsalts, the proportion of halogen in the chlorides corresponding to from under 1 p.c. to over 8 p.c. of the sub-chloride; in the iodide, corresponding to from 0·64 to 4·63 p.c.; and in the bromide sometimes corresponding to as much as 7 p.c. of the sub-salt.

The photochloride, which the bromine and iodine compounds resemble in general properties and methods of preparation, may be obtained in various colours, varying through salmon, pale pink, rose, copper-red, reddish purple, chocolate, and other shades, to black.

The following are some of the methods of preparation: (1) the chlorination of the metal, best by the action of a freshly prepared chlorine solution on freshly prepared colloidal silver, the salt in this case being of a rose-red colour; (2) the partial reduction of the normal chloride; (3) the reduction of silver oxide or carbonate by heat, with subsequent treatment by hydrochloric acid; (4) the treatment of the sub-oxide or a sub-salt with hydrochloric acid, followed by nitric acid; (5) the treatment of the subchloride with nitric acid or an alkaline hypochlorite; (6) the treatment of a solution of silver nitrate with ferrous, manganous, or chromous oxide, and treatment of the product with hydrochloric acid; (7) the treatment by hydrochloric acid of the product of the reduction of silver citrate in hydrogen; (8) treatment of a silver solution with potash or soda and a reducing agent, such as milk sugar, or any easily oxidisable body, the precipitate being treated with hydrochloric acid.

The photosalts are formed when the halogen salts of silver are allowed to remain in contact or are warmed with colloidal solutions of silver, the excess of silver being subsequently removed by solution in nitric acid. They are also obtained by adding a suitable reducing agent to silver nitrate, which is in contact with an ordinary silver halogen salt. The reducing agents recommended are (1) sodium citrate or potassium tartarate and ferrous sulphate; (2) tannic or gallic acid and alkali carbonate; (3) formaldehyde and sodium hydroxide; (4) sodium hypophosphite (Lüppo-Cramer, Zeitsch. Chem. Ind. Kolloide. 1907, 2, 135; *ibid.* 1908, 2, 360; *ibid.* 3, 33, 135).

Reinders (Chem. Weekblad. 1910, 7, 961) has prepared crystalline photochloride of silver by crystallising silver chloride from dilute aqueous solutions of ammonia in presence of sunlight. The crystals have an indigo-blue colour, the depth of tint depending on the intensity of the light and the duration of crystallisation. The darkest crystals contained 1 p.c. of free colloidal silver. The colour of the crystals undergoes various changes on exposure to light or to variously coloured glass.

These salts are permanent in the dark, but become purple or purplish-black when exposed to light. They are all decomposed by strong nitric acid, and slowly dissolve in ammonia, ammonium chloride, or sodium chloride, leaving a little silver. When heated, the photosalts are altered in colour, usually towards redness. Thus the grey salt may become pink at 100°, while the dark varieties may turn chocolate-colour or purple at that temperature.

Hydrogen peroxide also induces a series of colour changes in the photohalides from green to blue, then to red. The green salt contains most silver, and is least sensitive to light, whilst the red contains most silver and is most sensitive (Trivelli, Chem. Zeit. 1909, 33, 844; Chem. Weekblad. 1910, 7, 351; *ibid.* 404).

The action of light on the chloride, and similarly on the bromide and iodide, has been variously attributed to the production of metal, sub-chloride and oxy-chloride; and to the formation of a photochloride.

The evolution of chlorine under the action of light is indisputable, but the composition of the residue is still doubtful. Some chemists consider it to be a mixture of the normal chloride and silver, whilst others consider that the product in the case of silver bromide consists of the unchanged salt with a sub-bromide and metallic silver. Basing his conclusions on measurements of solubility of electrical potential, Sichling (Zeitsch. physikal. Chem. 1911, 771) considers the photochlorides to be solid solutions of silver chloride and amorphous silver, the half chloride Ag_2Cl is probably also present, but is of little importance in the system (Carey Lea, *l.c.*; Staats, Ber. 1887, 20, 2322; 1888, 21, 2199; Newbury, Amer. Chem. J. 6, 407; Tommasi, Bull. Soc. chim. [ii.] 37, 291; Abney, Proc. Roy. Soc. 33, 164; *ibid.* 40, 251; Griveaux, Compt. rend. 1888, 107, 837; Richardson, Chem. Soc. Trans. 1891, 536; Chem. Soc. Proc. 1898, 179; Eder, Chem. Zeit. Rep. 1899, 196; Abegg, Chem. Zentr. 1899, i. 649; J. Soc. Chem. Ind. 1900, 70; Baur, Zeitsch. physikal. Chem. 1904, 45, 613; Trivelli, Zeitsch. wiss. Photograph. Photophysik. and Photochem. 1908, 6, 358; Proc. K. Akad. Wetensch. Amsterdam, 1909, 11, 730; Lüppo Kramer, *l.c.*; *see* also article on PHOTOGRAPHY).

Hitchcock (Amer. Chem. J. 11, 474) found as much as 4·2–4·9 p.c. of chlorine eliminated from thin films of silver chloride exposed to sunlight in a *current of hydrogen.* Carey Lea (Amer. J. Sci. 38, 356) has shown that anhydrous silver chloride or iodide is darkened by light under petroleum, where the production of any quantity of oxychloride is impossible. Richardson has made a similar experiment with carbon tetrachloride (Chem. Soc. Trans. 1891, 544).

Regarding the action of dyes in modifying the sensitiveness of silver to different parts of the spectrum (orthochromatic photography) *v.* Vogel (Ber. 1873, 6, 1302); Eder (Sitz. Ber. 1884, 1117: Monatsh. 6, 1; 7, 1); Bothamley (J. Soc. Chem. Ind. 1887, 423; Brit. J. of Photography, 35, 499); Valenta (J. Soc. Chem. Ind. 1900, 375); Günther (*ibid.* 1905, 1083); Mees and Wrathan (Phot. J. 1906, 46, 300; D. R. P. 376051); *see* also PHOTOGRAPHY.

ORGANIC SALTS OF SILVER.

A number of organic salts of silver are employed in medicine as substitutes for silver nitrate, which is open to the objection of combining with the albumin and the sodium chloride of the tissue fluids forming an insoluble compound, and thus losing in penetrative power. These compounds possess great penetrability, are not precipitated by saline and albuminous solutions, and their aqueous solutions are generally not decomposed by weak acids, alkalis, alkali sulphides, or sodium chloride.

Silver citrate (*Itrol*) $Ag_3C_6H_5O_7$ is a white, odourless, heavy powder, obtained by precipitating a solution of silver nitrate with a solution of citric acid neutralised with sodium bicarbonate.

Silver lactate (*Actol*) $AgC_3H_5O_3,H_2O$ is obtained by dissolving silver carbonate in dilute lactic acid in the dark. It forms colourless needles, which turn brown rapidly on exposure to light.

Silver acetate $AgC_2H_3O_2$, prepared by the action of sodium acetate on silver nitrate, forms white, minute crystals of a disagreeable metallic taste.

Silver tartrate $Ag_2C_4H_3O_6$ is obtained as a white curdy precipitate on mixing solutions of Rochelle salt and silver nitrate. It is nearly insoluble in water, but dissolves in dilute ammonia. This solution deposits its silver as a shining mirror when gently heated, and under various modifications, and is largely employed in silvering glass. A good mixture is prepared as follows: (1) Dissolve 5 grms. of silver nitrate in 100 c.c. of distilled water and add ammonia until the precipitate first produced is nearly dissolved. (2) Dissolve 1 grm. of silver nitrate in 20 c.c. of water, heat to 43°, and add a solution of 0·83 grm. of Rochelle salt in 10 c.c. of water. Boil the mixture for 10 mins., filter, and dilute to 500 c.c. The glass, after washing with potash, dilute nitric acid, and alcohol, rinsing after the application of each, is covered with a mixture of equal volumes of these solutions at about 27°. After an hour the silver will have deposited in a coherent film, which may be polished or varnished after a few days (*v.* Cooley's Cyc. of Practical Receipts, 1872, 1044; Varley, Yearbook of Photography, 1890, 114).

W. H. Perkin (Chem. Soc. Trans. 1887, 362) describes an acid tartrate $C_4H_5AgO_6,H_2O$ crystallising in large brilliant monoclinic prisms, from a mixture of strong silver nitrate and tartaric acid solutions.

Silver fumarate $C_4H_2Ag_2O_4$ is precipitated as a white amorphous powder, requiring over 200,000 parts of water for solution, by addition of the acid or its salts to a solution of silver nitrate. It explodes on heating. Warnerke (Year-book of Photography, 1876, 131) has proposed its use in photography.

The crystalline double compound of **silver succinimide** and **hexamethylenetetramine** is obtained by dissolving the constituents in water, aqueous methyl, or ethyl alcohol or aqueous acetone, and warming the solutions *in vacuô* until crystallisation commences. The concentrated solutions of this compound are stable, are not discoloured by light, and do not coagulate albumin (D. R. P. 217897). Other silver double salts with hexamethylenetetramine, employed in medicine, have been prepared (D. R. PP. 193740, 213712, 209340).

Argentamine (*Ethylene diamine silver phosphate*) is made by dissolving 10 parts of silver phosphate and 10 of ethylenediamine in 100 of water. It forms a colourless alkaline solution not precipitated by chlorides or by albumin. Similar compounds are described in Fr. Pat. 400627, 1909.

When silver nitrate reacts with tetraethylammonium iodide a compound $(C_2H_5)_4NI,2AgI$ is formed. The substance is pure white, quite stable to light, and melts with very slight decomposition at 225°–230° to a light yellow liquid (Strömholm, Ber. 1903, 36, 142).

Silver phenol sulphonate $C_6H_4(OH)SO_3Ag$ is obtained by dissolving silver carbonate in *p*-phenolsulphonic acid, and evaporating to crystallisation in the dark. It forms colourless, odourless, prismatic crystals, decomposed by light, and when heated at 120°. It is soluble in aqueous alcohol, has a metallic taste, is antiseptic and non-corrosive, and, like itnol and argonin, is employed in eye diseases and for wounds (Zanardi, Chem. Zentr. 1898, ii. 712).

Argentol (*silver quin-aseptolate, silver oxyquinoline sulphonate*) $C_9H_5N(OH)SO_3Ag$ is a yellow powder sparingly soluble in water, alcohol, or in ether, more so in hot water. It is formed by the interaction of silver nitrate and sodium quinaseptolate. It is employed in medicine as a substitute for iodoform.

Argonin is a compound of silver and casein containing about 4 p.c. of the metal. It is prepared by adding silver nitrate solution to the sodium salt of casein and precipitating with alcohol.

Argyrol is a proteid salt of silver containing 30 p.c. of silver. It dissolves readily in water, forming stable solutions. It is employed for a variety of purposes in medicine, even strong solutions producing no pain or irritation (Nat. Stand. Dispensatory, 1905, 238).

Nargol is a compound of silver (10 p.c.) with nucleic acid derived from yeast. It is readily soluble in water and is used in the treatment of gonorrhœa, and in inflammation of the conjunctiva.

A soluble double compound of paranuclein and a silver salt is formed by adding the latter to an alkaline solution of paranuclein. Acid is added and the precipitate formed is dissolved in sodium hydroxide solution and then separated by evaporation (Eng. Pat. 4507, 1901).

Soluble silver nucleic acid compounds, having antiseptic properties, are formed by treating salts of nucleic acids with silver nitrate. The precipitate so formed is re-dissolved by the addition of a neutral salt such as sodium chloride, and the silver nucleic acid compound is isolated by precipitation with alcohol or evaporation *in vacuô* (Eng. Pat. 8407, 1906).

Protargol is a compound of protein and silver; it is a yellow powder with a weak metallic taste, soluble in water, and is said to be an excellent non-irritant bactericide.

Largin is a silver albumin compound containing 11·1 p.c. silver.

Silver also forms salts with acetylene (Maguire, J. Amer. Chem. Soc. 1906, 28, 1025; Mees and Wrattan, Phot. J. 1908, 48, 338).

If acetylene gas is led into a solution of silver nitrate acidified with nitric acid, a white precipitate is formed, which can be dried safely at 100°, is insensible to friction or percussion, but explodes violently when ignited. If potassium chlorate is added to the silver nitrate, the substance formed is also sensible to friction (Fr. Pat. 321385, 1902).

For other organic compounds of silver, *see* Eng. Pats. 26353, 1901; 23507, 1902; Fr. Pat. 380197, 1907; D. R. P. 218728; Charabot and March, Bull. Soc. chim. 1899, [iii.] 21, 552; Liebermann, Ber. 1902, 35, 1094; Kahlenberg, J. Phys. Chem. 1908, 12, 283; *ibid.* 1909, 13, 421; J. Chem. Ind. 1909, 707; Lüppo-Cramer, Zeitsch. Chem. Ind. Kolloide. 1908, 2, 325; Doughty, J. Amer. Chem. Soc. 1909, 41, 326; Angelli, Atti. R. Accad. Lincei. 1909, [v.] 18, ii. 38; *ibid.* 1910, [v.] 19, i. 784).

SILVER ASSAYING *v.* ASSAYING.

SILVERING is the art of covering the surface of bodies with a thin film of silver. This is now effected either by applying thin films of silver mechanically to the article to be silvered, or by the electro-metallurgical process. When silver leaf is to be applied, the methods prescribed for gold leaf are suitable. Among the metals, copper or brass are those on which the silverer most commonly operates. Iron is seldom silvered, but the process for both metals is essentially the same. The white alloy of nickel is now often plated.

The principal steps of this operation are the following:—

1. The *smoothing down* the sharp edges, and polishing the surface of the copper; called *émorfiler* by the French artists.
2. The *annealing*; or making the pieces to be silvered red hot, and then plunging them in a very dilute nitric acid till they are bright and clean.
3. *Pumicing*; or clearing up the surface with pumice-stone and water.
4. The *warming*, to such a degree merely as when it touches water it may make a slight hissing sound; in which state it is dipped in the very weak aquafortis, whereby it acquires minute insensible asperities, sufficient to retain the silver leaves that are to be applied.
5. The *hatching*. When these small asperities are inadequate for giving due solidity to the silvering, the plane surfaces must be hatched all over with a graving tool, but the chased surfaces need not be touched.
6. The *blueing* consists in heating the piece till its copper or brass colour changes to blue. In heating they are placed in hot tools made of iron, called *mandrins* in France.
7. The *charging*; the workman's term for silvering. This operation consists in placing the silver leaves on the heated piece, and fixing them to its surface by burnishers of steel of various forms. The workman begins by applying the leaves double. Should any part darken in the heating, it must be cleared up by the scratch-brush.

The silverer always works two pieces at once, so that he may heat the one while burnishing the other. After applying two silver leaves he must heat up the piece to the same degree as at first, and he then fixes on with the burnisher four additional leaves of silver, and he goes on charging in the same way, four or six leaves at a time, till he has applied, one over another, 30, 40, 50, or 60 leaves, according to the desired solidity of the silvering. He then burnishes down with great pressure and address till he has given the surface a uniform silvery aspect. A French patent (366785, 1906) describes a special process of preparing the silver leaf used in these operations.

Silvering by the precipitated silver chloride. The white curd, obtained by adding a solution of common salt to one of silver nitrate, is to be well washed and dried. 1 part of this powder is to be mixed with 3 parts of good pearlash, 1 of washed whiting, and 1½ of sea salt; or 50 parts of the chloride are mixed with 150 of potassium cyanide, 15 of aluminium nitrate, 50 thorium nitrate, 100 potassium bitartrate, 300 distilled water, and 350 of chalk (Fr. Pat. 320154, 1902). After cleaning the surface of the brass it is to be rubbed with a piece of soft leather, or cork moistened with water and dipped in the above powder. After the silvering it should be thoroughly washed with water, dried, and immediately varnished. Some use a mixture of 1 part of the silver precipitate with 10 of cream of tartar, and this mixture also answers very well.

Others give a coating of silver by applying with friction, in the moistened state, a mixture of 1 part of silver powder precipitated by copper, 2 parts of cream of tartar, and as much common salt. The piece must be immediately washed in tepid water very faintly alkalised, then in slightly warm pure water, and finally wiped dry before the fire.

Various other mixtures are employed thus: the silver chloride may be dissolved in aqueous sodium thiosulphate and the solution mixed with 8 p.c. ammonium chloride solution, ammonia and levigated chalk (Fr. Pat. 355518, 1905). A mixture of the chlorides of silver and iron, or copper, together with those of the alkaline earths or of magnesium or aluminium has also been employed (D. R. P. 118922).

Another process consists in the use of silver resinate. The latter is obtained by the interaction of an alkali resinate and a soluble silver salt in aqueous solution or by heating resin with an easily decomposable silver salt or with silver oxide. The silver resinate is dissolved in benzene and the solution is applied to the surface to be coated. The benzene is allowed to evaporate in the dark, and the article is then either exposed to the light for some time or treated with a solution of hydroquinone or pyrogallol in ethyl or methyl alcohol. The resin is then removed from the reduced silver by means of a suitable solvent. This process may also be used for plating the interior surface of articles (Fr. Pat. 380886, 1906).

The inferior kinds of plated buttons get their silvery coating in the following way:—

Two oz. of silver chloride are mixed up with 1 oz. of corrosive sublimate, 3 lbs. of common salt, and 3 lbs. of zinc sulphate with water into a paste. The buttons, being cleaned, are smeared over with that mixture and exposed to a moderate degree of heat, which is eventually raised nearly to redness, so as to expel the mercury from the amalgam formed by the reaction of the horn silver and the corrosive sublimate. The copper button thus acquires a silvery surface, which is brightened by cleaning and burnishing.

A mixture for silver plating, whereby cleaning, scouring, and plating are said to be carried out in one process consists of: 15 parts of silver nitrate converted into silver chloride by hydrochloric acid, 350–400 of tripoli powder or jewellers' rouge, or fine emery, 80–100 of acetic acid or vinegar, 300–350 sodium chloride or sodium nitrate, and 1 litre water (Eng. Pats. 14324, 6589, 1899). The unprepared article being rubbed with the mixture.

To produce a coating of silver on paper or leather, a mixture of ammonium silver nitrate and of a reducing salt (prepared by boiling aqueous potassium sodium tartrate with sugar) is applied to a glass plate, and the silver film formed is washed, dried, and covered with a warm solution of gelatin. The paper or leather to be coated is now laid on the film and rolled. After drying the film is stripped from the glass surface and adheres to the paper or leather (Eng. Pat. 20709, 1903; *see* also Eng. Pat. 4385, 1908).

To render the silver surface non-tarnishable the article is sometimes coated with a layer of zinc or other metal which will alloy with silver, but will not combine with sulphur. The article is then subjected to pressure by placing it into a closed cylinder into which a liquid such as petroleum or a solution of a salt of the coating metal is pumped (Eng. Pats. 25966, 1906; 16538, 16539, 18210, 1907; J. Soc. Chem. Ind. 1908, 947). Silver mirrors are sometimes protected with a film of celluloid (Perot, Compt. rend. 1909, 149, 725).

The silvering of glass for the manufacture of mirrors is carried out by a variety of processes, in most of which ammoniacal silver nitrate and some reducing agent are employed, but each worker seems to have his own recipe. The tartrates, however, give the most brilliant surfaces. The substances should be taken approximately in the proportions expressed by the following equation:

$$4AgNO_3+4NH_3+C_4H_4(KNa)O_6+H_2O$$
$$=2Ag_2+4NH_4NO_3+C_3H_2KNaO_5+CO_2$$

but the tartrate should be in slight excess.

A portion of the silver nitrate solution is mixed with the tartrate, warmed and filtered after the liquid has blackened. Ammonia is then added to the rest of the silver nitrate until the precipitate first formed is redissolved. The mixture of the two solutions deposits silver easily and uniformly. Before the deposition of the silver the glass surface should be prepared by washing with stannous chloride and rinsing with water.

The nature of the varnish employed to protect the film is also of great importance, as many substances are liable to attack the thin silver coating. Shellac is usually employed, but a mixture of resin with an insoluble base, such as zinc or magnesia, are said to be very good (Fafet, Rev. Chim. Ind. 1898, 9, 5). A process of silvering mirrors in which formaldehyde, together with glycerin, gum or sugar solution are used, is described in a Fr. Pat. (392243, 1908; J. Soc. Chem. Ind. 1908, 1204) (*v.* art. on ELECTROPLATING).

SILVER WHITE. *Blanc d'argent v.* PIGMENTS.

SIMILOR. A rich-coloured brass, said to be composed of 3 oz. of zinc to 1 lb. of copper.

SINALBIN $C_{30}H_{42}O_{15}N_2S_2,5H_2O$, a crystalline substance contained in white mustard seed (*Sinapis alba* [Linn.]), of a sharp taste, easily soluble in water, and converted by myrosin into sinalbin mustard oil, acid sulphate of sinapine and glucose (*v.* GLUCOSIDES).

SINAPINE *v.* GLUCOSIDES and VEGETO-ALKALOIDS.

SINAPOLINE *Diallyl urea* $CO(NH{\cdot}C_3H_5)_2$. A crystalline substance obtained by boiling mustard oil with baryta water or lead oxide.

SINIGRIN. A glucoside found in black mustard, easily soluble in water, slightly soluble in 96 p.c. alcohol, insoluble in amyl and *iso*butyl alcohols, ether, acetone, or chloroform, somewhat soluble in warm methyl alcohol, melts and becomes brown at 130°, gives a white precipitate with basic lead acetate in presence of ammonia, a yellowish-red colouration, but no evolution of mustard oil when boiled with 33 p.c. solution of potassium hydroxide. Hydrolysed by eryrosin, but by no other hydrolytic enzyme, with formation of allyl *iso*thiocyanate (Gonnermann, Pflüg. Arch. Phys. 1911, 137, 453; J. Soc. Chem. Ind. 1911, 30, 305).

SINODOR. A term for a basic magnesium acetate (*v.* ACETIC ACID; also MAGNESIUM).

SINTER. A name applied to incrustations on rocks or elsewhere, from mineral waters. According to the nature of the deposit, it is distinguished as calcareous sinter (travertine), silicious (quartz or opal), ferruginous (pitticite), arsenical (scorodite), &c.

SKIMMIN *v.* GLUCOSIDES.

SKUTTERUDITE. *Cobalt triarsenide v.* COBALT.

SLAG, BASIC, *v.* FERTILISERS.

SLATE. (*Ardoise*, Fr.; *Schiefer*, Ger.) A fine-grained sedimentary rock, usually argillaceous, characterised by a highly fissile structure. The fissility, termed *slaty cleavage*, is due to a rearrangement of the particles of the rock consequent on compression, and it has been shown by Sorby and others that the direction of cleavage is at right angles to that in which the pressure was applied; hence the planes of cleavage need not bear any relation to the original bedding of the rock. (For an able discussion of the subject of slaty cleavage *v.* A. Harker, in Rep. Brit. Ass., for 1885, 813.)

Most slates have originally been clayey sediments, and they consequently present much the same chemical composition as clays. It is notable that minute acicular crystals of rutile are often abundant. (On the origin of slate and of the rutile *v.* W. M. Hutchings, Geol. Mag. 1890, 264, 316; 1891, 164, 304, 459.) Many secondary minerals, particularly chiastolite, may be developed in slate, especially where it is invaded by igneous rocks, such minerals being commonly found in the zone of metamorphism around granite intruded into an area of slate.

The best slates occur in North Wales, where they have been worked since at least the sixteenth century. The principal quarries are those of Penrhyn, near Bangor, and Dinorwig, near Llanberis, where purple and green slates are worked in the Llanberis group of the Cambrian system. The slates quarried around Ffestiniog occur at a higher geological horizon, being referable to the Llandeilo beds. In Cornwall and Devon slaty rocks of Devonian age are abundantly developed, and have been extensively quarried at Delabole and Tintagel in North Cornwall.

Slates are not only valued as roofing material, but are used in large slabs for cisterns, flags, steps, tombstones, billiard tables, &c. Mantelpieces are often constructed of slate, and enamelled to imitate marble or serpentine. Minor uses of slate are for splitting into school slates and cutting up into slate pencils. For pencils a soft fine-grained material is required, but as only small pieces are used there is no disadvantage in the rock being broken up by joints and cleavage-planes. The Skiddaw slate of the Lake District is used for pencils. The green slates of the Borrowdale series of Cumberland, which are used for roofing, consist chiefly of fine volcanic ash, in which perfect cleavage has been developed by compression.

Although the term 'slate' should properly be restricted to rocks which exhibit superinduced cleavage, it is often extended to fissile rocks which split along the original planes of bedding. Such thin flaggy rocks occur in the Oolitic system, and though not so thin and light as true slates, are used for sake of their picturesque effect, especially in Gothic buildings. The *Stonesfield slates* of Oxfordshire and the *Collyweston slates* of Rutland are calcareous sandstones of this character. Such slates are not readily split into thin slabs when first quarried, but need exposure to a winter's frost in order to develop their latent fissility.

References.—J. A. Howe, The Geology of Building Stones, London, 1910. For the details of quarrying and dressing slate, *v.* D. C. Davies, Slate and Slate Quarrying, London, 1878.

F. W. R.

SMALT *v.* COBALT.

SMALTITE (*Speiskobalt*, Ger.). A mineral consisting essentially of cobalt diarsenide $CoAs_2$, of importance as an ore of cobalt. It has long been used for the preparation of smalt, hence the name smaltite. The crystals possess the same degree of symmetry as cobaltite (CoAsS) and iron-pyrites (FeS_2), but the pyritohedral faces are not often present, the form being usually the simple cube or the cubo-octahedron. Distinctly formed crystals are, however, exceptional, the mineral usually occurring as granular and compact masses. The percentage of cobalt required for the above formula is 28·2, but analyses rarely show over 20 p.c.; this is due to the isomorphous replacement of cobalt by iron and nickel, and as the nickel increases in amount there is a gradual passage to the isomorphous mineral chloanthite (*q.v.*). The colour is steel-grey, and the streak greyish-black. The material is brittle; H. 5½–6; sp.gr. 6·4–6·6. Heated in a bulb-tube it gives a sublimate of metallic arsenic. When weathered the mineral alters to erythrite (cobalt-bloom), the characteristic peach-blossom colour of which is very often to be seen as specks and stains on specimens of smaltite, thus affording an easy means of recognising the mineral.

Smaltite occurs, together with ores of nickel, silver, and copper, in veins traversing granite and gneiss at Schneeberg, Annaberg, and Freiberg in Saxony, Joachimsthal in Bohemia, Wittichen in Baden, &c.; and in 1903 a similar occurrence was discovered at Cobalt on Lake Temiskaming in Northern Ontario. In association with niccolite, barytes, and asbolite it occurs in veins traversing the Kupferschiefer (copper-slate) at Richelsdorf and Bieber in Hesse, and at Kamsdorf and Glücksbrunn in Thuringia. The occurrence of the mineral in the Saxon Erzgebirge led to the establishment long ago of cobalt colour works in this district. The still larger quantities recently found in Canada are far more than is required for the colour industry, and attempts have consequently been made to introduce metallic cobalt for the same purposes as nickel.

Safflorite is also cobalt diarsenide, but orthorhombic in crystallisation: it is thus dimorphous with smaltite and isomorphous with mispickel and marcasite. It occurs together with smaltite; in the massive form the two are practically indistinguishable, and no doubt the ordinary ore contains both minerals. The name 'safflorite' is from zaffre or safflor, a mixture of roasted cobalt ore and quartz used for colouring pottery. L. J. S.

SMELLING SALTS consist of mixtures of ammonium carbonate, or less often ammonium chloride, with a variety of essential oils. A large number of recipes are employed in their preparation, the following of which may be mentioned. Small glasses or bottles with ground glass stoppers are filled with pieces of sponge, previously well beaten, washed, and dried. These are then saturated with a mixture of ammonium chloride (9 parts) and oil of lavender (1 part); or the bottle may be filled with uniform sized pieces of ammonium carbonate and the above mixture poured over it. Other mixtures consist of: (1) 2 oz. ammonia water, 7 drops of oil of lemon, 2 of oil of lavender, 4 of oil of bergamot; (2) 4 oz. ammonia water, 15 minims. of oil of rosemary, 15 of English lavender oil, 8 of oil of bergamot, and 8 of oil of cloves; (3) a coarse powder of normal ammonium carbonate is sometimes perfumed with bergamot oil (0·56 drm.), lavender oil (0·9 drm.), nutmeg oil, clove oil, rose oil (0·78 drm. each), cinnamon oil (2·82 drms.). This preparation is known as *white smelling salts.*

Violet smelling salts; coarsely powdered ammonium carbonate is moistened with a mixture of 2½ oz. of concentrated tincture of orris root, 1 drm. of spirit of ammonia, 3 drms. of violet extract, or the moistened carbonate is treated with as much of a mixture of 5 minims. of oil of orris, 10 of oil of lavender flowers, 30 of violet extract, and 2 fluid oz. of ammonia water, as it will absorb.

Preston salt consists of a mixture ammonium chloride and freshly-slaked lime, to which a suitable perfume is added.

Antiseptic smelling salts; often used for colds, hay fever, &c., consist of the following mixtures: (1) 1 lb. ammonium carbonate, 2 fluid oz. ammonia solution, 4 fluid drms. eucalyptus oil, 1 fluid drm. lavender oil, 2 fluid drms. peppermint oil; (2) 120 grms. phenol, 1½ fluid drms. eucalyptus oil, 4 fluid oz. ammonia solution. (3) 10 parts menthol are dissolved in 78 parts of alcohol, and 12 parts of ammonia solution are added. Other antiseptic smelling salts are prepared by mixing 1 fluid oz. each of liquefied phenol, eucalyptus oil, iodine solution, and 2 fluid oz. of ammonia solution; or 360 grms. of ammonium carbonate, 120 of camphor, 480 of phenol, 1 fluid dram. of eucalyptus oil, 1 of lavender oil, and 2 of ammonia solution are mixed with a sufficient quantity of wood charcoal to form a suitable mass (*see* Encyclopædia of Receipts, Dick, 119; 20th C. Book of Recipes, Hiscox, 1907, 510; Chemisch. Technische Lexicon, Bersch, 1908, 630; Scient. Amer. Cyclopædia of Formulas, Hopkins, 1911, 873).

SMILACIN *v.* SARSPARILLA.

SMITHSONITE *v.* ZINC.

SMOKE and SMOKE PREVENTION. Smoke consists of liquids and solids condensing from heated products of combustion as they escape into the cool air, and in many cases solids carried from the burning mass by the uprush of heated gases. If the products of combustion are entirely gaseous no smoke is formed.

The character of smoke varies with its source, and in most cases the nose is able to detect the character of the burning material from the smell of the condensing vapours in the smoke, so that tobacco smoke, coal smoke, wood smoke, the smoke from green vegetable matter, rags, animal matter or gunpowder have such distinctive characteristics that the sense of smell at once differentiates between them.

It will also be noticed that the smell of smoke has great diffusive power; thus the odour from a burning heap of weeds may be detected at long distances, whilst a cigarette smoked in a ground-floor room can be detected throughout the house.

This, together with many other characteristics of smoke, is due to the form taken by the condensing liquids, which have a certain degree of viscosity, and which, as their vapour cools down, condense in the form of minute vesicles filled with air or products of combustion, and which continue to float until contact with some surface causes the bursting of the liquid envelope, which deposits as a minute drop, liberating its gaseous contents.

That this is so may be seen from an experiment devised by Mr. Hovenden, in which a puff of cigarette smoke drawn through a cell of suitable structure and illuminated by an arc light or oxy-hydrogen limelight from below can be examined by the microscope, when the vesicles are clearly visible and can be seen to be endowed with great activity.

Given proper conditions most condensing vapours appear to assume this form, and the small vesicular masses seem to retain the molecular activity of the particles that build them up, and there is little doubt that in fog or cloud it is this formation that gives the floating power, as the water vapour contained by the vesicle is only a little more than half the weight of air. It also explains the formation of rain by gun-fire and the dispersion of fog by electrical discharges, the bursting of the vesicle in each case leading to precipitation.

The form of smoke which is, perhaps, the most injurious, and to which we are most accustomed, is that produced by the use of bituminous coal as a fuel for manufacturing and domestic use, and which, with the growth in the population of the country and the prodigal methods of using the fuel, is creating in our large towns atmospheric conditions that are little short of a national scandal.

When in the thirteenth century bituminous coal was first used for fuel purposes, the smoke to which it gave rise roused such indignation that a decree was passed in 1306 forbidding its use; but fuel had to be found, and the supply of timber proving insufficient, once more attempts were made to introduce it, but again public opinion led to its banishment during the reign of Queen Elizabeth. The third attempt, however, to bring it into use proved successful, and slowly the consumption increased, until the last century saw coal firmly established, not only as a fuel for domestic consumption, but also as the great source of power, and it was the possession of great stores of the fuel that gave England her commercial supremacy.

It was only in the latter half of the last century that the cumulative effect of smoke began to make itself appreciable, and the eighties and nineties were marked by a diminution in the hours of sunshine in our big cities, and by fogs of remarkable density; but such legislation as was enacted, the efforts of those interested in smoke abatement, and the large increase that has taken place in the use of coal gas for cooking and fuel purposes, have apparently had some slight influence in a reduction of the plague. Certainly during recent years the fogs have not been of the same density or so frequent as in the preceding 20 or 30 years; but how far this has been due to efforts at smoke abatement, and how far to meteorological conditions, it is difficult to say.

The factor which makes it difficult to obtain complete and therefore smokeless combustion of coal in a furnace, and almost impossible in an ordinary grate, is that bituminous coals of the kind used as fuel decompose rapidly at temperatures above 400°, with the evolution of gases and condensable vapours, whilst a solid residue of carbon in the form of coke remains on the bars.

The gas is of the character of ordinary coal gas, and is easily burnt without smoke, whilst the coke residue also offers no difficulties, but the vapours, which on cooling condense to tar, are of so complex a nature, and under the influence of heat undergo such varied changes that their combustion is a most difficult problem, and it is the carbon, pitch, tar oils, and products from these that are the smoke-producing factors.

The period at which the densest smoke is emitted is in every case immediately after fresh fuel has been fed on to the fire, and in a furnace with properly-proportioned combustion space and carefully adjusted air supply and chimney draught, careful stoking or the use of automatic stokers will do much to reduce it; but in the domestic grate, where neither air supply nor draught can be properly controlled, and where the coal is put on in pieces often of considerable size and in quantity sufficient to prevent any further feeding being needed for a considerable time, the conditions for smoke production are at their best, and the loss of the calorific efficiency of the coal becomes so great that often less than 20 p.c. of the heat finds its way into the room.

The statements that have been made as to the loss of heat from the formation of smoke are so varied, and in many cases so excessive, that it will be well to consider the thermal actions taking place when bituminous coal is fed on to a clear fire.

A pound of ordinary bituminous coal, as used on the domestic fire, contains a total amount of heat equal to 14,000 B.Th.Us. On putting it on a bright fire there is at once a noticeable fall in temperature, and from the fresh coal streams of steam and brownish smoke will be seen to escape up the chimney, the temperature above the newly-charged fuel not being sufficient to ignite it. The brownish smoke consists of coal gas and tar vapour, and after half an hour the heat from below penetrates the distilling coal, ignites the escaping gas and tar vapour, and so gives a cheerful flame which radiates heat into the room.

The radiant heat from a flat gas flame is about 18 p.c. of the heat value of the gas, but when the gas is diluted with products of combustion and over-aerated by the rush of air inwards from the room, as is the case with an open fire, under the best conditions it rarely reaches 10 p.c., and as in a coal fire quite one-half of the gas evolved from the coal escapes up the chimney unburnt during the period when the top of the fire is at too low a temperature to ignite it, 5 p.c. of the heat of the gas evolved is a liberal allowance for the radiant heat from the flame above the fire.

The pound of coal distilled under the conditions existing in the fire, heated only from below and cooled by the air above, will certainly not yield more than 5 cub. ft. of 600 B.Th.U. gas, so that the heat radiated into the room from flame from the gas will not exceed 150 B.Th.Us. There will be 0·05 lb. of tar vapour, having a thermal value of 16,000 B.Th.Us. per lb. equal to 800 B.Th.Us., of which 5 p.c. again will be the most that is radiated, or, in other words, 40 B.Th.Us.

The burning mass in the grate has to supply the amount of heat necessary to decompose the coal, convert portions of it into gases and vapours, which are heated to the temperature of the mass and escape with that heat up the chimney; this will require 1200 B.Th.Us. over and above any endothermic heat due to the decomposition, whilst the evaporation and superheating of the moisture in the coal accounts for another 250 B.Th.Us.

Air has to pass through the burning fuel to support the combustion, and if it could be so perfectly regulated in amount as to be just about 150 cub. ft., then the residual nitrogen and the products of combustion would escape up the chimney, and would leave the zone of combustion heated to 760° C. (1400°F.), abstracting not less than 6000 B.Th.Us. The strong updraught in the chimney created by the flame and heated products draws in some 20,000 cub. ft. of air per hour over the fire, which, together with the grate and back of the fire, is to an extent cooled by it, a loss which may be included in the 6000 B.Th.Us.

In the burning coke remaining from the pound of coal there are left 2750 B.Th.Us., from which the walls of the grate and ashes will abstract another 265 B.Th.Us., and the residual amount radiated into the room will depend upon the temperature and brightness of the glowing mass, so that the most heat we can hope to obtain is 2485+150+40 B.Th.Us., equal to 2675 B.Th.Us. out of the 14,000 B.Th.Us. in the pound of coal, or 19 p.c., the other 81 p.c. having mostly gone up the chimney as waste heat, or unburnt in the mixture of tar vapour, steam, carbonaceous matter, gases and ash that is called smoke.

We can now make up the balance of heat for the coal fire as follows:—

			B.Th.U.
One pound of coal—			14,000
Lost 81 p.c.	In gas	2850	
	In tar vapour	760	
	Moisture	250	
	Decomposition and volatilisation	1200	
	Products of combustion	6000	
	Grate and ash	265	
Available 19 p.c.	Heat from fire	2485	
	Heat from flame	190	
			14,000

These figures, based on careful experiments, show that although the actual amount of heating value lost in the smoke itself is small, yet that the heat lost by using bituminous coal and forming smoke amounts to 4810 B.Th.Us., or a third of the heat in the coal.

If the products escaping from a fire soon after being fed with fuel be collected in the flue they are found to contain—

1. Tar vapour ;
2. Water vapour ;
3. Tarry carbon particles ;
4. Particles of ash ;
5. Gases ;

and the gases on analysis prove to be—

Carbon dioxide	0·70
Methane	0·36
Hydrogen	0·29
Carbon monoxide	0·01
Oxygen	18·85
Nitrogen	79·79
Sulphur acids	traces
Sulphuretted hydrogen	,,

showing the dilution that has taken place owing to the excess of air drawn over the fire by the chimney draught.

The tar vapour in the smoke is formed by distillation from the coal, whilst the solid carbon deposits coated with tar, which we call soot, are a secondary product of the incomplete combustion of the tar vapour, and are formed by the cooling of the flame above the fire by the air drawn in by the chimney draught, which also carries off from the fine particles of ash and coal dust.

The water vapour and gases, other than the nitrogen and oxygen, are formed by complete and incomplete combustion, and amongst them are to be found sulphur compounds, such as sulphuretted hydrogen and sulphur dioxide, the first formed during the distilling period when coal has just been fed on to the fire, and the latter during the combustion. Both these compounds are due to the sulphur always present in the coal, and whilst the former blackens white lead paint and tarnishes silver, the sulphur dioxide dissolving in water oxidises to sulphuric acid, which is far more actively injurious, corroding and destroying metal work and building materials, retarding the growth of vegetation and finally killing it.

Bituminous coal contains from 0·5 to 3·5 p.c. of sulphur, chiefly in the form of iron pyrites, and it is generally assumed that as about 16,000,000 tons of coal are used in London annually, the sulphur is all converted into sulphuric acid, and that anything from half a million to a million tons of acid is so formed in the air of London in the course of the year. This is undoubtedly an exaggeration, as during the smoke-forming period of combustion a large proportion of the sulphur comes off in combination with hydrogen, and escaping unburnt, can be detected in the chimney gases by its action on lead acetate paper, whilst some of the sulphur dioxide is removed by rain before the oxidation to sulphuric acid is completed.

The sulphur compounds in the air vary with the state of the atmosphere, so that on a breezy bright day, even in the heart of London, 100 cub. ft. of air may contain only 0·015 grs., whilst during a dense fog they may rise to 0·24 grs., and it is clear that as the smoke helps the formation of the fog, and this in turn prevents diffusion and removal of the impurities in the air, the prevention of smoke should go far towards purification of the town atmosphere.

Deleterious as is the effect of sulphuric acid in the air and rain upon the growth of vegetation, it is found that the soot in town air is even more so, as the small masses of spongy carbon that are called ‘ blacks ’ have the power of absorbing and concentrating sulphuric acid, so that they may contain 4–8 p.c. of it, and when the growing plant gets coated with a tarry film rich in ‘ blacks,’ not only are the functions of the pores of the plant deranged, but the acid is brought in a concentrated form in contact with the leaf surface.

Smoke once formed finds its way from the chimney into the atmosphere, and is rapidly diffused through the air by means of currents, and it is manifest that if there were no means of removing it, the air would soon become perfectly opaque from its accumulation in large quantities. When, however, rain falls it rapidly washes the air free from suspended solid and liquid impurities which constitute the visible portion of smoke. Snow is even more efficacious than rain in this respect ; where the snow has fallen on the glass roof of a greenhouse it will be noticed that when it melts it leaves behind a black deposit, consisting of the solid matter which it has collected during its passage through the air. An analysis of a deposit of this character formed on the glass roofs of some orchid houses at Chelsea serves to show the nature of these solid impurities—

Carbon	39·00 p.c.
Hydrocarbons	12·30 ,,
Organic bases	1·20 ,,
Sulphuric acid	4·33 ,,
Ammonia	1·37 ,,
Metallic iron and magnetic oxide	2·63 ,,
Other mineral matter, chiefly silica and ferric oxide	31·24 ,,
Water not determined.	

In cases where long drought prevents the rapid clearance of the air by this means, the heavier of the solid particles settle by gravity, whilst the particles of carbon and carbonaceous organic matter are slowly oxidised by the oxygen and ozone into carbon dioxide, in which form vegetation removes them from the air.

The solid particles suspended in air are, however, by no means confined to the products of our improper use of bituminous fuel, and mineral matter from the dust of roadways, and organic matter from animal and vegetable life, play their part in rendering town air deleterious to health, but it is the smoke ‘ dirt ’ that is the most injurious factor.

The smoke from our grates is naturally discharged at a lower level than that from factory shafts, with the result that it probably has a greater effect on our general health and buildings than the higher layers of smoke, which travel for miles with the wind, and which act more by darkening the sky and cutting off the sun’s rays. It is also clear that the low-level smoke will not extend so far from the point at which it is formed, as contact with buildings and vegetation rapidly robs it of the tar vapours, with the result that in a smoky town like Leeds it has been shown that at 1 mile away the solid impurities have fallen to one-half, and at 2½ miles to one-sixth.

Injurious as are the direct effects of smoke on health and property, they are small as compared with those brought about by dense fog, which may to a great extent be attributed to smoke, partly by helping its formation and partly by retarding its dispersion.

Fog, whether it be in the form of white mist which is found in the country, or the yellow variety which we know so well in towns, is formed by the condensation of water vapour from the air, and this is brought about by any cause which rapidly cools a large volume of moist air. If, instead of the surface of the ground and the objects on it only being cooled, the air for a considerable height above it is also lowered in temperature, then the moisture which is deposited from it, instead of forming dew, condenses in the air, forming minute vesicles that remain suspended and float in the air, constituting fog or mist. In pure air the mist so formed consists of little else than these minute bubbles of water, and has no irritating effect on the eyes or lungs. In a large town like Leeds, however, the air is charged with an enormous number of minute particles, the heaviest of which settle on a horizontal or roughened surface in the form of dust, whilst the lighter particles continue floating in the air. These particles consist of a heterogeneous collection of all kinds of matter, amongst which 'smoke' particles bulk largely, constituting more than one-half. All these floating solids cool with great rapidity on account of the smallness of their size, and in so doing cause the rapidly-cooling air to deposit moisture upon them, and so aid in the formation of the town fog, which appears long before the country mist.

The air of towns where much coal is used also contains the volatile tarry matter distilled off during the imperfect combustion, and this condensing with the moisture coats it on the outside with a thin film, which does much to prolong the existence of the fog, as when the temperature of the air again rises, the clean mist once more evaporates into the atmosphere, but the tar-coated yellow fog has its power of evaporation retarded to an enormous extent. Experiments made by Sir E. Frankland show that the evaporation of water in dry air is reduced nearly 80 p.c. by blowing some smoke from burning coal on to its surface.

Many estimates of the relative amount of pollution due to manufactories and to the domestic grate have been made, but as the question of what is the ratio of smoke production from the various sources varies enormously with the locality, no very satisfactory conclusion has been arrived at.

With regard to London, Dr. Shaw's estimate that 70 p.c. of the smoke is due to the domestic fire would probably be about correct, but in Sheffield or Birmingham the figures would most likely be reversed. Domestic smoke is produced throughout the whole length and breadth of the land, whereas the factory chimney is to be found mainly in the more limited area of the manufacturing districts.

Although it is difficult to gain any idea of the ratio of blame to be given to the two greatest sources of smoke-production at any one spot, it is easy to obtain an insight as to the relative total amount of smoke so produced from the uses to which our coal is put, and the Royal Commission on Coal Supplies arrived at the conclusion that of the 167 million tons of coal burnt in this country in 1903, 36 millions were used for domestic heating, whilst, after deducting the coal used for gas making, it would probably be nearer the truth to say that the domestic use of bituminous coal is responsible for one quarter of the smoke pollution of the country, the responsibility for the remainder being split up amongst the various manufactures and railways.

Practically all the advances of late years have been in fuel consumption on the large scale, and the improvements brought about by stoking machinery and attention to air supply have been great, whilst some of the largest manufacturers have demonstrated not only the ease of obtaining smokeless factory shafts, but also the economy that accompanies them.

The methods that could be adopted for reducing the production of smoke from domestic sources are :—

1. The use of bituminous fuel in special grates ;
2. The use of solid smokeless fuel ;
3. The use of gaseous fuel ;
4. The combined use of gas and coke ;
5. Central heating by steam, water, or hot air.

In considering the claims of these various methods we must remember that the English open fire is undoubtedly the most comfortable and wasteful method of heating that could be adopted ; but although by far the largest proportion of the heat escapes up the chimney, we must clearly bear in mind that this very factor makes it a most important engine of ventilation. Moreover, it heats the room in the only healthy way, that is, the radiant heat from it does not directly raise the temperature of the air, but is radiated to the floor, walls, and furniture in the room, which again part with their heat slowly to the air in contact with them and to the inhabitants, so that the walls and other solid matters in the room are at a higher temperature than the air.

Apart from its being more healthy to breathe cool than hot air, there is another important point to consider. The normal temperature of the body is 98°F., or 36·8°C., and this temperature is maintained by the slow combustion processes going on in the body. By the laws of radiation a heated surface parts with its heat more or less rapidly according to the temperature of the surrounding bodies, so that if a person be sitting in a room filled with warm air, but near a wall colder than the air, his body will rapidly part with heat by radiation to the wall, and a sensation of chill is the result ; but with the open fire this is never the case, as the radiant heat from the fire heats the walls of the room to a temperature higher than that of the air. But when a room is heated by means of hot-water pipes or warmed air, the walls not being heated in the same proportion, although the air may feel warm, the walls will remain cold, so that the heat of the body would pass by radiation to the walls and give rise to a chill.

If, therefore, we can retain the chief characteristic of the open fire—heating by radiation—and eliminate the smoke production and excessive waste of heat up the chimney, we should have the ideal conditions for house-warming.

Great improvements have been made in the domestic grate during the last 15 years, both from the artistic and economic point of view. Whilst with the older forms it was not unusual to find a coal consumption of 7–8 lbs. of coal per hour, this quantity has been reduced in the more modern forms to about one-half. This in itself has been an important step in smoke reduction; but grates have long lives, and the capital outlay of putting in new ones results in the modern forms being found chiefly in new houses. There have been many attempts made to construct grates for the smokeless consumption of coal, but it is found in practice that when once the heavy carbonaceous smoke is produced, it is very difficult to again burn the carbon particles completely, and the dilution caused by the large volumes of nitrogen present prevents their easy combination with the oxygen of the air.

Stoves have been constructed in which the coal should be supplied to the bottom of the fire so as to keep the top bright and clear, all the smoke having to pass through the clear fire above, where it is decomposed. Such grates are by no means novel, as one of the best was the 'Arnott,' and must be over 60 years old; but for some reason they have never been popular with stove manufacturers, with the result that they have never reached the public, otherwise they are efficient and economical.

The great factor in making special forms of grate an inefficient solution of the smoke problem is that it involves large capital outlay on the part of the consumer, and it is for this reason that the use of solid smokeless fuel, which can be used in all existing grates, appears the most likely solution of this important question.

Smokeless fuels may be classified as—

1. Coal which has been carbonised at a high temperature so as to drive out practically all the volatile matter, and this class is represented by gas coke and Coalexld.
2. Coal which has been partially carbonised so as to distil out the smoke-forming constituents, but to leave enough volatile matter to give a non-luminous flame and easy ignition, as seen in Coalite and Carbo.
3. Non-bituminous coal, such as anthracite.

The waste of heat due to the actions taking place when coal is used has already been fully dealt with, but if, instead of using bituminous coal and polluting the atmosphere with the products of its incomplete combustion, the gasworks be allowed to conduct the first and most wasteful part of the process and to carbonise the coal in the manufacture of illuminating gas, ammonium sulphate and tar, and the coke be burnt in the grate, it is found at once that we save the 2850+760+1200=4810 B.Th.Us. used in the formation of smoke, which then become available for the purpose of radiating into and warming the room, so that the amount of heat is more than doubled, whilst the only loss to be placed against it is the 190 B.Th.U. which radiation from the flame gave when coal was used.

Coke has never found favour with the upper and middle classes as a domestic fuel, probably because it is somewhat difficult to ignite and does not burn freely. Its chief market has been for horticultural work, and for steam-raising and other manufacturing purposes, very little finding its way into the householder's grate. The result is that, had not carburetted water-gas offered a convenient and economical means of using it in gasworks, many companies would have found great difficulty in keeping up the price during the years that coal was cheap.

It has been shown that in an open grate consuming bituminous coal the heat lost in the volatilisation and decomposition of the hydrocarbons, *i.e.* in the production of smoke, is considerable, but that if coke is used this heat remains in the residue and is radiated into the room, so that a much hotter fire results, and with a good chimney draught coke gives a bright fire which has more than double the heating effect on the room that can be obtained from an ordinary coal fire.

If, however, the draught is sufficient only to burn coal with its more easy ignition and more rapid burning, the coke gives a dull and unsatisfactory fire with a tendency for traces of the products of combustion to escape the feeble suction of the chimney and pass into the room, due to there being little or no flame to start the chimney draught.

Since the almost universal adoption of the incandescent gas mantle high candle-power gas has become unnecessary, and in gas manufacture the greatest yield of gas from the coal has been obtained by using very high temperatures in the carbonisation. This, by driving out all the volatile matter from the coke, has made it still denser and less easy of ignition.

This phase of gas manufacture is, however, passing away, and the most modern methods of procedure and the use of vertical retorts, chamber carbonisation, and heavy charges are all tending to yield a form of coke more fitted for domestic consumption, and as a very little attention to the form of stove and chimney draught would burn it in a satisfactory way, every attempt should be made to popularise its use, as it gives at once a smokeless and economical fuel.

Coalexld is a smokeless fuel, made by mixing a very small proportion of alkaline nitrates with the coal before carbonisation, and these decomposing, give small traces of oxygen and create small areas of very high temperature in the body of the coal, so giving a slight increase in the yield of gas; but as will be seen from the analysis of the coke formed, it contains a trace less volatile matter than the ordinary coke from the same coal, and as it is upon this that ease of ignition and freedom in burning depend, it is difficult to see how it can be a better fuel than good coke.

'Charco' is another coke fuel, made by cooling the hot coke as it is drawn from the retort by smothering the combustion with a layer of coke breeze, instead of quenching it by water in the usual way.

The following analyses give the composition of coke, coalexld, and charco made from the same coal—

	Coke	Coal-exld	Charco
Moisture (after air drying)	1·83	1·08	0·83
Proximate analysis (on dry sample)—			
Volatile matter	4·37	3·13	2·66
Ash	5·98	5·86	5·43
Sulphur	0·48	0·43	0·40
Calorific value—			
On dry coke, calories	7765	7651	7615
Calculated on combustible	8256	8131	8058

The second class of smokeless fuel, and the one which many scientific men look upon as the most promising solution to the smoke problem, owes its inception to Colonel Scott-Moncrieff, who in 1880 suggested the use of half-coked coal as a fuel supply, and tried to make a commercial article by carbonising coal at the ordinary gas-retort temperature, drawing the charge when half the usual volume of gas had been distilled from it. Two factors, however, led to failure, the one being that the time was not ripe, and the second that the means by which he proposed to carry out his entirely admirable idea, being dependent upon the ordinary gasworks practice, had to be carried out under such conditions as led to a want of uniformity in the fuel and to certain difficulties which those who tried to make it failed to overcome.

The idea, however, of a semi-carbonised coke, which should still contain enough volatile matter to give easy ignition and a cheerful flame without any smoke, was independently revived in 1907 under the name of 'Coalite.'

Coalite differed from the fuel proposed by Colonel Scott-Moncrieff in that, instead of shortening the period of carbonisation at a high temperature, the temperature was reduced to one-half the ordinary, and was continued in suitable retorts until a uniform coke, containing 12–15 p.c. of volatile matter was formed.

The coalite process had the great advantages over the older process that the fuel was of greater uniformity, and that the yield of tar was doubled instead of being decreased, and was greatly enhanced in value.

Coalite created so much interest that, as was only natural, the Moncrieff process was revived, and the product is well known under the name of 'Carbo.'

The use of a non-bituminous coal like anthracite would result in smokeless and very hot combustion, but here again the objection is that stoves with a special draught would have to be used, and the initial cost would prevent its ever being adopted; besides which, any great demand for this kind of fuel would at once send up the price of the fuel to a prohibitive figure.

If the consumer can be induced to take the trouble, a very good semi-smokeless fuel can be made by using a mixture of two-thirds coke to one-third coal, and instead of piling up the grate with cold fuel when the fire burns low, to add the fresh fuel frequently in small quantities, so as to prevent the deadening of the top heat of the fire. But this is diminishing not killing the evil of smoke production.

Leaving the smokeless solid fuels, which in the future will play a great part in the cleansing of town air, the next possible solution of the smoke problem lies in the use of gaseous fuels, and here at once there is ready to hand the use of coal gas. Gas fires, gas cookers, gas water-heaters, and gas engines have been developed to a point which leaves no valid excuse for overlooking their claims, and ever since Bunsen in the early fifties gave the world the atmospheric burner, in which non-luminous and smokeless combustion is obtained, coal gas has steadily progressed in favour for heat and power as well as light, until at the present time nearly as much of it is used for the one purpose as for the other.

Although much has been done by the gas companies in popularising gas stoves by letting them out on hire, by easy payment systems, and by looking after their maintenance, the consumers must pay something, and that is sufficient to damp their ardour as smoke reformers, whilst gas is also a little more expensive for continuous heating than coal, although when used for short periods, as for fires in bedrooms, &c., the fact that the gas is turned on when the fire is wanted, and turned off when it is done with, the saving in labour and the cleanliness bring the fuel cost to nearly the same as coal, whilst in such places as Widnes and Sheffield, where the price of gas has been reduced to a minimum for heat and power, the gas engine and gas fire well hold their own.

An excellent suggestion, made first by Sir W. Siemens, is to decompose bituminous coal into coke, tar, and gas at the gaswork, and to re-unite the true heat-producers, coke and gas, in the fire grate without the smoke-producing tar. All the initial outlay needed for this is to fit the atmospheric burner arrangements of the gas stove to any ordinary fire grate, so arranging them that they can be made to swing back clear of the fire when they have done their work of bringing to bright combustion the gas coke used as fuel in the grate. This has always seemed to be the most economical method of using the products of gas manufacture, because it would be impossible to use either gas or coke alone to entirely supplant the use of bituminous coal; a market must be made for the by-product if prices are to be kept down, and as it may be hoped still further reduced, but if the use of both gas and coke could be increased, the gas manager could afford a diminution in the price of tar from over-production. V. B. L.

SMOKELESS POWDER *v.* Explosives.

SOAP. The term 'soap' in its widest sense includes all salts of fatty acids. In ordinary language, as also in commerce, the term is applied almost exclusively to that mixture of alkali salts and water which is sold as soap.

It is most convenient to sub-divide the soaps into the two main classes, viz. (1) *Salts of the alkali metals; water-soluble soaps.* (2) *Salts of the alkaline earths and heavy metals; water-insoluble soaps; metallic soaps.*

Ammonia soaps, which as yet are of no great commercial importance, would be classed with the water-soluble soaps.

(1) Salts of the Alkali Metals; Water-Soluble Soaps.

According as to whether the base used for the saturation of the fatty acids be soda or potash, we differentiate between *hard soaps* (soda soaps) and *soft soaps* (potash soaps). The former may contain small quantities of potash soaps (as is the case in high-class shaving and other soaps), whilst the latter may also contain some proportion of soda (as is the case in soft soaps made in summer), but it is convenient to found the classification on the quantity of the preponderant base, as, indeed, is done in practice.

The fatty raw material for commercial soaps may be furnished by any oil or fat of vegetable or animal origin. Thus an enormous variety of soaps can be, and, indeed, are produced on a large scale. But not every oil and fat yields a soap fulfilling the demands made on it for household, toilet, and manufacturers' purposes. Broadly speaking, it may be stated that the vegetable drying oils and marine animal oils are, on account of their consistence, best suited for the manufacture of soft soaps. Also some of the semi-drying oils (maize oil, rape oil) lend themselves especially for this purpose. Solid fats are used preponderantly for making hard soaps; into this category fall also the non-drying oils. Semi-drying oils, as typified by cotton seed oil, may be used as stock material in admixture with other suitable oils and fats for both soft and hard soaps.

The art of the soap-maker consists in blending the raw material at his disposal in such a manner as to produce that soap which is most suitable for a given purpose.

Rosin is largely used in conjunction with fatty material in the manufacture of both hard and soft soaps.

1. Hard Soaps—Soda Soaps.

The earliest processes of manufacturing hard soap (described by Pliny) consisted in boiling oils and fats with causticised wood ashes, the potassium carbonate contained therein being converted into caustic potash by boiling with lime. The potash soaps so obtained were converted into soda soaps by treating the soap paste repeatedly with common salt.

Later on the wood ashes were replaced by 'soda ashes' obtained by burning seaweeds ('barilla,' 'kelp'). The manufacture of sodium carbonate by the Leblanc- and the ammonia-processes almost completely extinguished the use of barilla and kelp, and the soap-maker was thereby enabled to obtain manufactured soda (soda ash, sodium carbonate), which he causticised himself in the same manner as that employed for wood ashes. Thus the caustic soda required for the saponification of oils and fats was actually manufactured in the soap works, and is, to a large extent, still being produced by the soap manufacturer.

The development of modern chemical industry led to the production of solid caustic soda in alkali works (commenced in England, 1850), so that the soap-maker has at present the choice of either buying caustic soda in the solid form or himself manufacturing caustic soda solution ('caustic lyes') from soda ash, by causticising sodium carbonate, and subsequently concentrating the dilute caustic soda solution in vacuum evaporators of simple or multiple type (for illustrations, *see* GLYCERIN).

The following two processes for the production of hard soaps from oils and fats on a manufacturing scale are chiefly in use: (A) *Soap-making by the cold process*, and (B) *Soap-making by the hot process.* Recently a third process has been introduced on a limited scale, viz. (C) *Soap-making by double decomposition of lime soaps and sodium carbonate.*

Under the head of 'hot process' falls also the method of making soap from fatty acids or 'soap stock fatty acids.'

For the theory underlying the process of soap-making from oils and fats, *see* GLYCERIN and SAPONIFICATION.

The theory of soap-making from fatty acids is expressed in its simplest form by the following equation, wherein R denotes the radicle of any suitable fatty acid—

$$R{\cdot}OH + NaHO = R{\cdot}ONa + H_2O.$$

For the physical properties of the soaps of the several fatty acids, their solubility, their behaviour towards water (*hydrolysis of soap*), caustic alkalis, carbonate of the alkalis, glycerin, alcohol, and neutral salts, the reader must be referred to the article OILS, FIXED, AND FATS and to Lewkowitsch, Chem. Techn. vol. i. 99–114.

(A) *Soap-Making by the Cold Process.*

The oils and fats most suitable for the manufacture of soaps by the cold process are those belonging to the cocoa-nut oil group, as they possess the property of being converted into soaps on being stirred together with concentrated caustic soda solutions of approximately the sp.gr. 1·35. The plant required for this manufacture is of the simplest construction, and merely consists of an iron or wooden frame into which the fat, previously brought to a temperature of about 35°, is placed; the fat is then stirred, whilst an accurately measured quantity of caustic soda of sp.gr. 1·35 is run in. The frame is covered and allowed to stand, when the mass develops some heat, sufficient to complete the process of saponification within 24 hours.

The simplicity of this process naturally led to the market being flooded with 'cold' soaps prepared by unskilled operators, so that these soaps contained a considerable excess of caustic soda, or unsaponified fat, side by side with free caustic soda. The prejudice which has arisen against this class of soap is, however, unfounded, as it is not difficult, by careful working, to prepare practically neutral soaps. For this purpose the quantity of caustic soda required for saponification must be calculated from the saponification value of the fatty material.

These soaps are not readily 'salted out' by brine; hence they can be used for washing with sea-water (*marine soaps*). By incorporating with cocoa-nut oil certain proportions of olive oil, lard, tallow, &c., these oils and fats can also be saponified in the cold.

Soaps so prepared naturally contain the whole amount of glycerol that results from the saponification of the oils and fats. The theoretical composition of a soap made from cocoa-nut oil, having a saponification value of, say, 240 by the cold process is the following—

Fatty anhydrides . .	54·50 p.c.
Combined sodium oxide Na_2O	8·86 „
Glycerol, water, and small quantities of inorganic salts (by difference) . .	36·64 „
	100·00

Cold soap cannot be conveniently made on a practical scale from fatty acids or soap stock fatty acids, as in consequence of the immediate combination of fatty acid with caustic soda, lumps are formed which occlude the uncombined materials. For this reason, fats containing notable amounts of free fatty acids are unsuitable for the manufacture of cold soaps.

Castor oil simulates the fats belonging to the cocoa-nut oil group by being able to form 'cold' soaps. The further property of castor oil of imparting translucency to soap has also been made use of in the manufacture of inferior cold soaps, and complete transparency is obtained by the addition of sugar solutions together with sodium silicate solution. On the Continent large quantities of cheap transparent soaps of this kind are made. They must not be confounded with the high-class transparent soaps described below.

(B) *Soap-making by the Hot Process.*

In soap-making by hot processes, either natural oils and fats or the fatty acids derived therefrom are used.

(a) *Soap-making from natural oils and fats with caustic soda.* The process of soap-making by boiling glycerides with caustic soda solutions is used on the most extensive scale, and is practically the only process which yields soaps of uniformly good quality, colour, and hardness, and at the same time the largest amount of glycerol obtainable from the raw material by means of comparatively simple operations.

In this process the oils and fats are introduced into a cylindrical or square iron vessel —soap kettle, soap 'copper,' soap pan—and churned up by means of steam, when a dilute caustic soda solution is run in, which assists the emulsifying of the fat and induces rapid hydrolysis.

It is necessary to commence with a dilute solution of caustic soda, as in the case of oils and fats, with the exception of the oils belonging to the cocoa-nut oil group and of castor oil, a strong solution 'cuts' the soap-paste, much as does salt solution.

The mass in the soap-pan at this stage consists of a mixture of soda salts of the fatty acids with water, in which the glycerol formed in the course of hydrolysis and the excess of caustic soda are dissolved.

It is necessary to employ an excess of caustic soda to obtain complete saponification. Experiments made by the author with his assistants Clapham and De Greiff have shown that by using the theoretically required quantity of caustic soda an equilibrium is established between soap and unsaponified fat so that the resulting mass contains such notable quantities of unsaponified fat that the soap would be unsaleable.

In order to convert the soap-paste into commercial soap, it is necessary to separate the soda salts of the fatty acids from the excess of caustic soda and of water by adding salt, whereby the soda soaps are thrown up. On allowing to stand, two layers are obtained: (1) a lower aqueous layer, containing salt, glycerol, and excess of caustic soda; (2) an upper curdy mass of soap granules, retaining about 30–35 p.c. of water. The lower layer is drawn off, and worked up for the recovery of the glycerol contained in it (*see* GLYCERIN). The curdy soap granules left in the pan are boiled up with water ('closed'), so as to form a homogeneous paste, which is again boiled with a little caustic soda to ensure complete saponification, and again separated into two layers in the manner described above. The soap is once more treated in the same manner, to remove impurities which impair its colour; in some cases it is boiled with a somewhat concentrated solution of caustic soda ('strengthening change') and 'salted out' again to a 'curd.' Finally the 'curd' is 'fitted,' *i.e.* brought into the condition of finished soap.

The art of the soap-maker consists in so 'fitting' the soap that it contains just the proper amount of water (which may be called the 'water of constitution,' *see* below), and is still 'open' enough to allow the intermingled heavier aqueous solution, as also the impurities (which consist to a notable extent of metal [iron, copper], salts of fatty acids) to settle out. After the mass has been allowed to rest for a few days, there is found at the bottom of the soap-pan a small amount of alkaline solution (which has separated out on cooling, *see* below), above which rests a layer of dark soap, intermixed with salt solution, containing the excess of caustic soda used. The dark colour is chiefly due to metallic soaps. This layer is termed in practice 'nigre' (*i.e.* black, a term taken from the Marseilles soap-makers). Above this rests the bulk of the finished soap, 'neat soap.' It is covered on the top by a thin layer of solidified soap of a spongy nature, owing to the occlusion of air which, on rising gradually to the top of the mass during settling became entangled there on cooling.

The excess of caustic alkali in the 'neat' soap should be very small; its amount depends on the care used in the manufacturing operations.

The finished 'neat' soap, whilst still warm, is run into soap crutching (mixing) machines (holding from 12 to 15 cwts. of soap), wherein perfumes and colouring matters are incorporated with the soap (if desired), and thence into soap frames, in which the warm mass is allowed to cool. (In the south of Europe the finished soap is run on to a cemented floor divided off by boards into suitable compartments, about 12–14 ins. high. For the best class of household soaps the cemented floor is covered with paper.)

The soap in the frames requires a few days to solidify. The sides of the soap-frames are then removed, and thus a rectangular soap block is left. This block is cut at first into slabs which are then divided into bars and tablets, and thus placed on the market.

The process of solidification of the soap being a somewhat lengthy one, there have been introduced recently cooling machines, which, whilst new, enjoy, especially on the Continent, a certain vogue. In this country, however, such cooling machines have found very limited use. For the best household soaps the process of cooling in frames has maintained its supremacy.

Pure commercial soda soaps made by the process described contain practically 30 p.c. of water, and no more than 63–64 p.c. of fatty acids. Such a soap is termed 'genuine soap.' The theoretical composition of a genuine soap made from neutral glycerides having the mean molecular weight of about 860 (tallow, olive oil, &c.), is as follows—

Fatty anhydrides . . .	61·60 p.c.
Combined sodium oxide, Na_2O .	7·18 „
Water, including small quantities of inorganic salts and glycerol (by difference) . . .	31·22 „
	100·00

In the course of a long series of experiments which the author carried out on a large scale on many tons of varied fatty materials, with the object of producing a commercial soap having a higher proportion of fatty acids than 63–64 p.c., he was never able to obtain a commercial soap of the desired higher percentage. Hence, the author adopted the view that this proportion of water might be termed 'water of constitution,' inasmuch as a commercial soap having less water cannot be obtained in the soap-kettle.

The statement made by Merklen that he obtained soaps with higher percentage than 63–64 p.c. has been refuted by the author as impossible (*see* Lewkowitsch, J. Soc. Chem. Ind. 1907, 590; Jahrbuch d. Chem. xvii. 415; Lewkowitsch, Chem. Techn. iii. 259).

(b) *Soap-making from fatty acids* ('*Soap stock fatty acids*). This process of soap-making was first suggested by Chevreul, and has, indeed, been in practical use ever since the stearine candle industry was established, the manufacture of soap from oleic acid—the by-product of the stearine candle industry—affording a natural outlet for this by-product. Since fatty acids are capable of expelling carbonic acid from sodium carbonate when boiled in aqueous solution, soap can also be made by boiling fatty acids with sodium carbonate.

The initial manufacturing operation is, therefore, practically tantamount to neutralising the fatty acids with caustic soda or with sodium carbonate, as the case may be. The precaution must, however, be taken that the aqueous solution of caustic soda or sodium carbonate is put first into the soap-pan, and that the oleic acid is allowed to run in slowly whilst the mass is kept boiling, so as to avoid formation of lumps of soap. If sodium carbonate be used, the boiling must be conducted with great circumspection, so as to facilitate the evolution of carbonic acid and to prevent boiling over of the fobbing mass.

In consequence of the high price which glycerin has reached, special 'deglycerinising' works were established on the Continent, and the manufacture of soap from 'soap stock fatty acids' has gained some extension, notably in small soap-works on the Continent, one of the chief advantages claimed for this raw material being the saving of cost afforded by using sodium carbonate in place of caustic soda—of course, as far as the proportion of free fatty acids permits.

The soap stock fatty acids are prepared by the saponification processes mentioned under Nos. 2, 5c, and 6 in the article SAPONIFICATION.

The neutralisation of the soap stock fatty acids is carried out in the same manner as described above for oleic acid. The soda solution must be heated first in the soap-pan, and the soap stock fatty acids are introduced in small quantities, care being taken not to run in a further quantity before the carbonic acid has escaped so far that frothing over is prevented. It follows, of course, that the soap-pan must be of much greater capacity than is required for the same amount of soap made by the process described under (a), as ample space must be allowed for the tendency of the effervescing mass to rise rapidly. It is of the utmost necessity to keep the mass well boiling. Some operators even pass a current of air through the boiling mass in order to facilitate the escape of the carbonic acid. This contrivance cannot, however, be recommended.

When all the carbonic acid has practically escaped, the amount of caustic soda required for the saponification of the neutral fat is introduced; the boiling is then continued, and the soap further treated in exactly the same manner as described above.

Having regard to the exaggerated statements that are made by interested parties as to the advantages resulting to the soap-maker by working with soap stock fatty acids instead of with natural oils and fats, the fact should be emphasised that soaps of the best quality are obtained only by boiling glycerides with caustic soda, as described under (a).

With regard to the merits or demerits of the several soap stock fatty acids, it may be added that the autoclaved material has a paler colour than the material obtained by the Twitchell process, but an inferior one to that made by the ferment process. The loss of fatty material in the Twitchell process is practically *nil*, in the autoclave process it is very small, whilst in the case of the ferment process it is no longer negligible, a notable amount being lost in the middle layer. The soaps obtained from material prepared by the Twitchell process are the darkest. For this reason this process cannot be recommended for making 'genuine' soaps; it is essentially a process that produces material for low-class soaps. The most suitable material for making soap stock fatty acids by the autoclave process is that which is almost neutral, whilst raw material, high in free fatty acids, is better adapted for being worked up by the Twitchell process. Material rich in free fatty acids, especially in volatile acids, is not suitable for the ferment process, which works best with good raw material (like the autoclave process). However, it must be pointed out that tallow and other high-melting fats are unsuitable for the ferment process, and if these materials are required, they must be 'softened' by the admixture of low-melting fats, in order to become accessible to the action of the ferment.

None of these processes has been able to displace the boiling of neutral glycerides; nor are they likely to do so in the near future. Although one or the other, or all of the three processes may be worked on a small scale, they are only employed for dealing with special material adapted to the making of special soaps, and those of inferior quality. Many installations erected for the production of soap stock fatty acids have been laid idle within the author's experience, after practical results had demonstrated that first-class soap could not be obtained from such material.

(C) *Soap-making by Double Decomposition of Lime Soaps with Sodium Carbonate.*

The initial operation employed for the saponification of oils and fats have been described under SAPONIFICATION (No. 1 'Saponification by means of lime in the open vat') as the modification worked out by Krebitz. The lime soap obtained is transported to the soapery, and introduced in small quantities into a soap-pan containing a 'boiling' solution of sodium carbonate. When the decomposition of the lime soap is nearly complete, a small quantity of caustic soda solution is added. The soap-paste is next treated with salt, until the curd is thrown out. The contents of the soap pan are then allowed to rest, when calcium carbonate settles out at the bottom of the pan as a heavy sludge, whereas soap curd separates on the top; a salt solution containing an excess of alkali forms an intermediate layer. The calcium carbonate sludge is drawn off, and, as it holds soap entangled (from 4 to 7 p.c.), it must be washed, and finally lixiviated with water in a filter press, to recover the occluded soap. The soap left in the pan after drawing off the spent lye is reboiled, and finished in the same manner as described above under (a).

This process is an extremely cumbersome one. The manifold operations prior to the soap-making proper, and the repeated washings of the sludge necessary to recover the entangled soap, entail manipulations which compare very unfavourably with the simplicity of the 'hot' process described under (a).

Several years ago (when prices of glycerin were high) the process was adopted by some small Continental soap-works, which up till then had run their spent lyes to waste. As the caustic lime exercises some purifying action in the case of low-class material (such as bone fat) containing albuminoids and gluey matter, this process may continue to be practised with low-class material, under certain favourable commercial conditions.

DIFFERENT QUALITIES OF HARD SOAPS.

The 'genuine' soaps are, with special reference to the process by which they are made, termed in technical parlance '*settled*' soaps.

Next in purity to the genuine soap rank those soaps which are '*boiled on a lye*' and are termed 'curd' soaps. They are 'fitted' in such a manner that a somewhat open-grained soap 'curd' rests on a lye, which, in the case of the best class of soaps, consists of a salt solution containing only small amounts of caustic soap or sodium carbonate. The water in these 'finished' soaps contains larger quantities of salt than is the case with genuine soaps, and, therefore, the percentage of fatty acids barely reaches 63 p.c. If the fatty raw materials and the lyes are pure a separation of dark soap (impurities) between lye and soap cannot take place; but if the fatty materials, &c., are somewhat impure, a small layer of dark soap separates between the 'curd' and the lye. This layer is left in the pan to be dealt with in a subsequent operation. If the fatty material used in the making of curd soaps is of somewhat low quality (kitchen grease, bone fat, &c.) it is necessary to finish on lyes somewhat strong in caustic alkali. The impurities, such as metallic soaps, &c., segregate on cooling in the form of veins in the soap, and cause the solidified soap to exhibit a slight 'marbling' or 'mottling.' These soaps are, therefore, known as 'genuine mottled' soaps. The proportion of fatty acids in the soap is about 61 p.c.

A lower quality still than 'genuine mottled' soap is the type represented by the so-called 'Marseilles soap.' The Marseilles soap contains less than 60 p.c., as a rule not more than 57 p.c., of fatty acids. In order to give it sufficient hardness for handling, it must be 'pickled' in a brine solution. In the author's opinion a soap of this kind must be classed as a 'filled' soap. The manufacture of this soap is practically confined to Marseilles; and even there the demand for it is greatly diminishing.

The repute which this soap enjoyed led to the production of another kind of mottled soap, with which the Marseilles soap must not be confounded, and which, in the author's opinion, must be looked upon as an 'adulterated' soap. This imitation Marseilles soap, known as 'blue mottled' soap ('Eschweg soap,' 'Nantes soap'), is still a 'fitted' soap, inasmuch as its proportion of fatty acids is a definite one, lying between 46 and 48 p.c., and cannot be varied at will (as is the case with the soaps to be described below). This soap is made by 'filling' the genuine soap-paste with solutions of sodium carbonate, sodium silicate, and (or) salt, which vary both in strength and in their several proportions according to the nature and composition of the fatty raw material used. This soap represents at the boiling temperature a mixture of two soap solutions, so carefully balanced by the art of the soap-maker that they have approximately the same specific gravity at a temperature slightly below the temperature at which the soap has been 'finished.' Hence, on solidification of the mass, no separation of the components into two distinct layers takes place. What separation does take place occurs so slowly that the solution which is richer in soap solidifies and imprisons the solution which is poorer in soap, before the latter has had time to segregate in the form of a lower layer. Hence the desired 'marble' in the soap is obtained. The marbling is made more pronounced by the addition of ultramarine or 'copperas' for blue-mottled soap; by using other pigments, lamp black and 'English red,' grey mottled and red mottled soaps respectively, are produced. Such soap also requires 'pickling' before it is put on the market. The soap can be boiled direct from neutral fats in one operation, when, of course, the glycerin remains in the soap. But it is more profitable to the soap-maker to remove the bulk of the glycerin by saponifying the whole or part of the fatty material in a separate pan, thus obtaining a 'glycerin lye' and curd soap, which is then converted into mottled soap. The colour of the finished soap does not suffer thereby, whereas soap made from 'soap stock fatty acids' frequently becomes so seriously discoloured that it is practically unsaleable.

The lowest kind of 'fitted' soaps are those which are termed 'semi-boiled' soaps. These soaps are nothing but more or less concentrated saline solutions of soap, and can be made to contain any desired proportion of water. Some kind of purification is effected by allowing these soaps to drop a certain amount of 'nigre,' containing a good deal of the impurities in the raw material; but, as a rule, these soaps are filled into frames immediately after being made. The manufacture of these soaps may be considered as entirely obsolete, all the more so as the glycerin contained in the fatty raw material is lost, much as in the making of best soft soap from glycerides; indeed, these soaps may be likened to soft soaps. At present small quantities of this class of soap are still made in the south of Europe from low-class fatty material, rich in free fatty acids. This kind of soap must, of course, be considered an 'adulterated' soap.

In this country 'adulterated' soaps are mostly prepared by the aid of the mixing (crutching) machines into which 'neat' soap settled on a nigre is run, and is there incorporated with solutions of salt, sodium carbonate, and (or) sodium silicate to any desired extent, so that all grades of soap ranging from 60 p.c. of fatty acids downwards to even 10 p.c. can be, and are, made. In order to give those soaps sufficient firmness for handling they are either 'stoved' or 'pickled,' as the case may be.

In mitigation of the practice of 'filling' soaps with solutions of sodium borate, or of sodium carbonate or (and) silicate, is adduced the apologetic explanation that, besides hardening the soap, the added solutions possess detergent properties. The best that can be said for soaps of this class, which range in their proportion of fatty acids between 52 and 60 p.c., is that they might be considered as standing on the borderland between genuine soaps and 'adulterated' soaps. They should be openly described as 'filled' soaps.

There can, however, be no doubt that adulteration has taken place in the case of those 'filled' soaps which have been 'loaded' with weighting substances, such as clay, talcum (sold as 'fillers'), chalk, barytes, asbestos, seed husks, &c., or with solutions of magnesium salts, &c. In the same category fall soaps filled with starch. In the opinion of the author soaps containing less than 50 p.c. of fatty acids should be looked upon as 'adulterated,' whether the 'filling' have detergent properties or not, unless the admixture be declared openly ('sand soaps').

Special kind of soaps for toilet purposes are *remelted soaps, milled soaps,* and *transparent soaps.* For the manufacture of these the reader must be referred to Lewkowitsch, Chem. Techn. iii. 275.

2. Soft Soap—Potash Soap.

In the manufacture of soft soap the base used preponderantly is potassium hydroxide, small quantities only, if any, of caustic soda being employed under certain conditions. Thus in summer it is the custom to saponify with a mixture of caustic potash and caustic soda, according to the desired consistence of the finished product. The manufacture of potash soap is much simpler than that of hard soaps, as it involves practically only one operation, viz. 'boiling' the glycerides with caustic alkali solutions in a pan, no 'salting out' being required. Hence the resulting product, after being properly 'fitted,' can be run straightway from the boiling-pan into the vessels in which the soap is sold.

The method of manufacturing 'genuine' commercial soft soap for household purposes differs, however, essentially from that employed in the manufacture of hard soap, in that the presence of potassium carbonate is required so as to produce a soap of clear translucent appearance which possesses the desired consistence for handling.

Soft soap used to be made in fire-heated pans; but during the last two decades these have been replaced in modern works by pans similar to those used in the manufacture of hard soap, and fitted with a 'close' steam coil in addition to an open steam coil or coils.

The fatty raw material which for the best soap consists chiefly or preponderantly of linseed oil, is introduced into the soap-pan and churned up with steam, when a caustic potash solution of about 20° Tw. is run in. Whilst the saponification proceeds, lyes of higher strength can be used. When all the glycerides have been converted into soap, and the latter is just slighly alkaline, potassium carbonate solution is introduced. The soap will then contain an excess of water; this is removed by turning off the open steam and heating the mass with the aid of the close steam coil. At the same time the mass is agitated by a suitable mechanical arrangement so as to promote the rapid evaporation of the excess of water. By taking samples and examining their appearance and consistence on a glass plate, the operator is able to judge exactly the point at which the soap is 'finished.' The mass then represents practically a mixture of potassium salts of fatty acids with a solution containing all the glycerin from the fats, a slight excess of caustic potash, and a certain amount of potassium carbonate. The two component parts of this mixture are so carefully balanced that, on cooling, a homogeneous mass is obtained which retains its transparency. If the soap is made from linseed oil only, the transparency will be retained even in winter, and the soap will not 'congeal'; but if the soap stock contains notable amounts of cotton seed oil, or even maize oil, and frost sets in, then the soap is liable to become dull ('blind'). Hence the choice of raw material is conditioned by the seasons. If some tallow is used in the stock, the harder potassium stearate or palmitate, or a mixture of both, crystallises out in star-like clusters, producing what is known in commerce as 'figging.' The same effect can also be obtained by replacing a portion of caustic potash by its equivalent of caustic soda.

In the soft soaps prepared in the manner described above all the glycerol is retained, and, as has been pointed out already, a certain excess of caustic potash and notably of potassium carbonate, necessary in order to give the soap the inviting appearance the public demands.

By operating carefully, potash soaps can be made which are devoid of free alkali and potassium carbonate. Such soaps are, however, only manufactured for the purposes of the textile industry, or 'liquid' soaps for cosmetic purposes, when absence of free alkali or of carbonate is essential, and the appearance of the soap is of no importance. In this case it is indispensable to work with pure caustic potash, as all impurities, such as sulphates, chlorides, and carbonates, pass into the finished soap.

The composition of a genuine potash soap made from fats having the mean molecular weight 860 is, theoretically, as follows:—

Fatty anhydrides . . .	38·700 p.c.
Combined potassium oxide, K_2O	6·843 „
Glycerol, water, and potassium carbonate (by difference) .	54·457 „
	100·000

Rosin is used for cheaper kinds of soft soap, just as in the case of hard soap. In the manufacture of soft soaps for textile purposes rosin must be avoided; and the presence of rosin in such a soft soap must be considered as distinctly lowering its value, or even as constituting adulteration.

Soft soaps, like hard soaps, are also 'filled' ('thinned out') with solutions of potassium silicate, potassium carbonate, potassium chloride, carragheen moss decoction, starch, and potato flour. The last two substances are largely used for the adulteration of opaque (white) soft soaps made on the Continent, especially the German 'silver soap,' in order to 'increase the yield.'

In the best soft soaps all the glycerol is retained, and its presence helps to impart to the soap the desired transparency. The endeavour to recover the glycerol has led to the production of soft soap from fatty acids (oleic acid and from 'soap stock fatty acids'). The production of soft soaps from these materials has gained ground, notably on the Continent. But the same strictures which have been made above with regard to hard soap made from such material may be repeated also in this case. High-class soft soaps, such as are in demand in this country, cannot be obtained with soap stock fatty acids. Whereas the fatty acids obtained by the Twitchell process are entirely unsuitable for soft soap, those made by the autoclave process can only be used for the inferior qualities. Slightly better than the soap stock fatty acids prepared by the autoclave process is the soap stock material obtained by the ferment process. It should, however, be emphasised that such soaps are inferior to those made from glycerides. As the price of potassium carbonate is almost the same as that of caustic potash, or slightly higher, it would be unremunerative to neutralise the free fatty acids in the soap stock fatty acids with carbonate, as is done in the case of hard soaps made from this material. There is, therefore, no inducement to use potassium carbonate in place of caustic potash.

Commercial varieties of soap. In order to suit various purposes, the variety of soaps that are being made is exceedingly great.

By far the largest quantities of hard soap are used for laundry, toilet, and other household purposes.

The most suitable soaps for laundries are either genuine mottled or 'settled' tallow-rosin soaps. The best class of *toilet* soaps contain, as a rule, 80 p.c. of fatty acids; but it must be understood that there are all varieties in commerce, down to the cheap transparent toilet soaps, which contain even less than 40 p.c. of fatty acids. Frequently medicaments, &c., are incorporated and thus an enormous variety of *medicated soaps* is made.

Special objects are served by *floating soaps*, made by incorporating air with soaps whilst still in the pasty state; *disinfecting soaps*, containing carbolic acid, formaldehyde, &c.; *sand soaps*, which are made chiefly from finely-ground silica or infusorial earth, by mixing it with hard soap (and sometimes with soda), so as to allow the mass to be shaped and handled like a soap cake.

During the last decade *shredded* soaps, made from genuine soap, and *ground* soap, also made from genuine soap, have come into vogue. These soaps may be considered as representing the best class of *dry* soaps. Usually, however, under the name of *dry soap* are understood those *washing powders* and *soap powders* which are prepared by grinding together hard soaps with sodium carbonate. Recently *perborates*, *persulphates*, &c., have been introduced into these soap powders under the plea that they add a bleaching effect to the washing effect.

Textile soaps are used in the textile industries, notably in the silk, woollen, and cotton industries, and form, as it were, a special group requiring brief consideration. In the silk industry the soap used for degumming the raw silk fibre is mostly made from olive oil or (chiefly in America) from lard oil. In the woollen industries soap is used (*a*) for scouring raw wool, (*b*) for scouring spun yarn, and (*c*) for scouring the woven woollen fabric; in the cotton industry it serves to remove 'stiffenings' and is used for washing the dyed or printed fabric.

Special kinds of *textile soaps* are *dry cleaning soaps* (benzine soaps), *soap emulsions*, prepared by partially neutralising Turkey-red oil with caustic alkali (such soaps are now frequently mixed with carbon tetrachloride or chloroethylenes), '*softening*' ('cotton softener') consisting of a salve-like emulsion made by incorporating large quantities of water with genuine soap.

The facility with which foreign substances can be incorporated with, and are retained by, solidified, jellified, or liquid soap has led to the production of an enormous amount of all kinds of 'special' soaps, for each of which some valuable property (real or supposed) is claimed. It is quite impossible to give a classification of these, and it must, therefore, be left to the analyst to decide, in each individual case, whether a soap containing foreign substances must be considered to be an adulterated soap or not. Thus a soap sold as a sand soap is not adulterated soap. Nor would a soap containing *naphtha*, or *petroleum*, or *tar oils*, or *sulphur*, or *peroxides*, or *perborates*, &c., fall under this head, if sold as *naphtha soap*, *petroleum soap*, *tar soap*, &c. It should, however, be pointed out that, as a rule, these substances are very frequently accompanied by loading materials (especially sodium silicate solutions).

Valuation and analysis of soap. In the valuation of soap, chemical analysis must play a prominent part, inasmuch as only thereby is it possible to ascertain the percentage of real soap, the amount of other constituents, and the presence of foreign substances. Whilst chemical analysis will thus be resorted to in the first instance, it must not be forgotten that a host of other factors, such as appearance, consistence, lathering properties, &c., play an important part in enabling one to arrive at a definite opinion as to the value of a soap. Not every soap is suitable for a given purpose, and much depends, *ceteris paribus*, on the nature of the fat stock which has been employed.

In what follows the most trustworthy chemical methods applicable to the examination and valuation of commercial soaps, are described. No attempt is made to indicate a complete course of analysis embracing the search for all substances that may possibly be present, as such a course would be of little practical use.

Sampling of soap. Great care must be exercised in sampling soap in order to avoid serious errors in the determination of water. On exposure to the air soap dries on the surface; and once a 'skin' is formed the outer portions of a cake protect to some extent the inner portions from loss of water by evaporation. In the case of hard soap, the sample for analysis should, therefore, be taken from the centre of the cake by cutting away all the outer portions; to what extent this must be done will be gathered by inspecting a transverse section, this showing to what depth drying has taken place. Such devices as taking a sample by means of a cork-borer, or by cutting a transverse slice from a cake, in order to obtain an 'average' sample, lead to erroneous results. If the sample under examination be a freshly made soap (containing about 30 p.c. of water), a fairly large portion should be weighed off rapidly, as the soap is apt to give up perceptible quantities of moisture to the dry atmosphere of the balance case. For the same reason the sample should not be sliced before weighing, except perhaps in the case of a milled toilet soap or of a thoroughly dried-out soap. The well-known contrivances for preventing loss of moisture during weighing must be resorted to, if highly-watered soaps be under examination.

(a) *Determination of Fatty Matter and of Total Alkali.*

Weigh off accurately 5–10 grms. of the sample (or 50 grms. on a balance sensitive to centigrams) and dissolve in hot water in a beaker or porcelain basin by heating gently; stir continually with a glass rod so as to prevent the soap from caking on to the bottom of the vessel. Add a few drops of methyl-orange and run in gradually hydrochloric, or dilute sulphuric acid (or dilute nitric acid if chlorides and sulphates are to be determined), until there is an excess of mineral acid. Heat with constant stirring, until the separated fatty acids have melted into oily drops; add about 5 grms. (or 20 grms. for 50 grms. of soap) of dry beeswax, or paraffin wax, weighed accurately on a tared watch-glass (which is used afterwards for weighing the fatty matter), and heat again until the mixture of fatty matter and wax has collected on the top of the liquid as a clear transparent oily layer, free from specks. Rinse off the glass rod with boiling water, heat until the fatty matter has again collected into one mass, remove the vessel from the source of heat, and allow to solidify by cooling. A white precipitate on the bottom of the beaker will indicate the presence of silicate or of 'fillings' insoluble in mineral acids.

The solidified cake is then detached from the vessel by means of a platinum spatula, lifted out of the liquid, rinsed off with cold water, and placed on filter paper. Any small quantity of fatty substance adhering to the sides of the vessel is carefully scraped off and added to the cake. Dry the cake (by touching lightly with filter paper), place it on the watch-glass used before, bottom side upwards, allow to dry in a desiccator and weigh. (For the control of works' operations, when 50 grms. should be used, it is sufficiently accurate to weigh immediately after drying with filter paper, taking care that no moisture remain in the cavities, if any, of the cake.) Should the cake contain any cavities (which only occurs when the fatty matter has not been heated properly) enclosing water, and perhaps even mineral acid, the fatty matter should be remelted in a basin over water, taken off after cooling, and dried as described above.

From the weight thus found the weight of the wax is deducted, and the difference returned as *fatty matter.* If no closer examination is made, it is, as a rule, returned as *fatty acids.* This is, however, only correct if the absence of neutral fat, wax, and unsaponifiable matter has been proved, *rosin acids* being looked upon as so much fatty acids, unless their separate determination is desired. With regard to the soluble fatty acids in soap, *cf.* Lewkowitsch, Chem. Techn. iii. 289.

If by subsequent examination the soap be found to be free from neutral fat, wax, and unsaponifiable matter, the fatty matter is returned as *fatty acids.* In a complete soap analysis the fatty acids are calculated to anhydrides by multiplying their percentage number by 0·9675.

The more fatty acids a sample contains, the more actual soap is present.

(b) *Combined Alkali, Free Caustic Alkali, and Alkaline Salts.*

The total alkali is the sum of the several amounts of alkali present in the soap as (1) alkali combined with fatty (and rosin) acids, termed conveniently 'combined' alkali; (2) free caustic alkali; (3) alkali as carbonate, or (and) silicate, or (and) borate.

In case of hard soap the alkali is calculated to Na_2O, and in the case of soft soap to K_2O.

If a separate determination of soda and potash be required, the soap must be decomposed with hydrochloric acid, and the potash in the acid liquid estimated as potassium platinic chloride.

(1) **Combined alkali** is usually found by difference, *i.e.* by subtracting the sum of the amounts of alkali obtained for (2) and (3) from the total alkali as determined above. It can, however, be found direct by titrating the alcoholic solution of the soap with normal acid, using methyl-orange as an indicator after neutrality has been established to phenolphthalein. This may be done as a check, or in order to dispense with the determination of the alkali present as carbonate, silicate, and borate (3), which obviously can then be found by difference.

(2) **Free caustic alkali.** A preliminary test is made by dropping an alcoholic solution of

phenolphthalein on to a freshly-cut surface of the soap. Pink colouration indicates the presence of free caustic soda (also of carbonate, silicate, and borate if the soap be moist). If the soap has dried out, the alkaline salts do not redden the phenolphthalein. In order to separate free caustic alkali from any alkaline salts, a portion of the sample is dissolved in absolute alcohol and filtered. The alkaline salts remain on the filter, so that the alcoholic filtrate may now be titrated, using phenolphthalein as an indicator.

Free caustic alkali should be absent from well-made soaps, especially from toilet soaps. As a great deal of circumspection and experience is required so to 'fit' a soap that it contains practically no free alkali, most of the ordinary commercial soaps will be found to contain an excess of free alkali. If this be small, the free caustic soda is mostly converted into carbonate on exposure to the atmosphere, so that in many cases no free alkali will be found, especially if only the outer portions of a cake be tested.

Free caustic alkali is determined quantitatively by dissolving 10–30 grms. of the sample in hot absolute alcohol in a flask, loosely corked in order to prevent absorption of moisture from the air. Highly-watered soaps must be first dehydrated to some extent, whilst access of carbon dioxide is excluded. The hot solution is filtered rapidly, care being taken that no soap-jelly separates out on the filter; if the operation is carried out judiciously, a hot-water funnel can be dispensed with. The filter is washed with absolute alcohol, and the filtrate received in a narrow-mouthed flask. Phenolphthalein is then added, and the solution titrated with decinormal hydrochloric acid. In some cases the alcoholic soap solution may exhibit an acid reaction to phenolphthalein. Acidity may be due to the soap containing an acid stearate (palmitate or oleate) owing to faulty 'fitting' or to fatty acid having been added to 'kill' an excess of alkali. The amount of decinormal alkali required to neutralise the solution is calculated to free fatty acids, in terms of oleic acid.

(3) The precipitate left on the filter contains carbonate, silicate, and borate, with which other insoluble substances, added as 'fillers' (starch, talcum), as also colouring matters, may be admixed. (With regard to the complete examination of this precipitate, *see* below.) To determine the alkali contained in the alkaline salts, the precipitate on the filter is washed with cold water, and the filtrate is titrated with standardised acid, using methyl-orange as an indicator. The acid used is calculated to Na_2O.

(c) *Determination of Water.*

The direct determination of water in soaps is, as a rule, an unnecessary operation. In the case of genuine soaps it suffices for all practical purposes to calculate the fatty acids to anhydrides, and add their weight to the amounts of alkali in its various forms. The water is then found by difference.

The direct determination of water is, therefore, only resorted to in exceptional cases. The soap is cut into fine shavings, brought into a porcelain dish, and weighed with a glass rod, so that the skin which forms on drying and prevents the escape of water from the inner portions may be conveniently broken up from time to time. This is especially necessary in the case of highly-watered soaps.

(d) *Examination of the Fatty Matter* ('Soap Stock').

If no wax has been employed in the separation of the fatty matter, the latter may be used direct for the following tests. Otherwise a fresh quantity of fatty matter must be prepared; the 'cuttings' are most conveniently used up for this purpose.

The fatty matter may contain besides fatty acids, (1) rosin acids, (2) neutral fat, (3) unsaponifiable matter.

(1) **Rosin acids.** Rosin acids are detected qualitatively by the Liebermann-Storch reaction. Their quantitative estimation (Twitchell's method) is based on the property aliphatic acids possess, of being converted into their ethylic ester when acted upon by hydrochloric acid gas in their alcoholic solution, whereas colophony undergoes very little change under the same treatment. The analysis is carried out as follows:—

Two to three grms. of the mixed fatty and rosin acids are weighed off accurately in a flask, dissolved in ten times their volume of absolute alcohol (with weaker alcohol the conversion of fatty acids into esters is not complete), and a current of dry hydrochloric acid gas passed through the solution, the flask being cooled by immersion in cold water. The gas is rapidly absorbed at first, and after about 45 mins., when unabsorbed gas is noticed to escape, the operation is finished. To ensure complete esterification the flask is allowed to stand for an hour, during which time the ethylic esters and the rosin acids separate on the top as an oily layer. The contents of the flask are then diluted with five times their volume of water, and boiled until the aqueous solution has become clear. From this stage the analysis may be carried out either (a) volumetrically or (b) gravimetrically.

(a) *The volumetric method.* The contents of the flask are transferred to a separating funnel, and the flask is rinsed out several times with ether. After vigorous shaking the acid layer is run off, and the remaining ethereal solutions, containing the ethylic esters and the rosin acids, washed with water until the last trace of hydrochloric acid is removed. 50 c.c. of alcohol are then added, and the solution is titrated with standard caustic potash or soda, using phenolphthalein as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain practically unchanged. Adopting 346 as the combining equivalent for rosin, the number of c.c. of normal alkali used multiplied by 0·346 will give the amount of rosin acids in the sample.

(b) *The gravimetric method.* The contents of the flask are mixed with a little light petroleum, boiling below 80°, and transferred to a separating funnel, the flask being washed out with the same solvent. The light petroleum layer should measure about 50 c.c. After shaking, the acid solution is run off, and the petroleum layer washed once with water, and then treated in the funnel with 45 c.c. of a one-fifth normal solution of KOH and 5 c.c. of alcohol. The petroleum solution of the ethylic esters will then be found to float on the top, the rosin acids having been extracted by the dilute alkaline solution with formation of rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids are collected as such, or preferably are dissolved in ether and isolated after evaporating the solvent. The residue, after drying and weighing, gives the amount of rosin acids in the sample.

(2) **Neutral fat.** A well-made soap will but rarely contain unsaponified fat. If neutral fatty substances have been added to the finished soap, as in the case of 'super-fatted' soaps (admixed with olive oil, &c., or, in the case of certain toilet soaps, with wool wax), they will be obtained together with any unsaponifiable matter present, and must be separated from it subsequently.

The neutral fat *plus* unsaponifiable matter is isolated in a direct manner from the sample of soap by dissolving a weighed quantity in water or alcohol, adding standardised caustic potash to neutralise free fatty acids (if any) phenolphthalein being the indicator, and exhausting the soap solution (*see* OILS, FIXED, AND FATS; *Determination of unsaponifiable matter*).

(3) **Unsaponifiable matter.** This is isolated and estimated together with neutral fat. If no neutral fat has been found, the total ether residue consists of unsaponifiable matter. This is examined as described under *Examination of the unsaponifiable matter* under OILS, FIXED, AND FATS.

In addition to the substances mentioned, the presence of vaseline, paraffin oil, oil of turpentine, tar oils, naphthalene, petroleum hydrocarbons, hydrocarbons from 'distilled grease,' &c., may be suspected.

Examination of the fatty acids. The examination of the fatty acids themselves, after separation from rosin acids, neutral fat, oxidised acids (if any), and unsaponifiable matter (*see* OILS AND FATS), with a view to determining the nature of the 'stock,' is a complicated problem, requiring systematic application of the methods described in the article OILS AND FATS, under the heading *Examination of fatty acids.*

(e) *Substances insoluble in Alcohol.*

The estimation of all those substances which are insoluble in alcohol is conveniently combined with the determination of free caustic alkali, by collecting the insoluble matter on a tared filter previously dried at 100°, and weighing after drying at 100°.

Good soaps yield but insignificant amounts of residue. Only transparent soaps manufactured by the 'alcohol process' will be found absolutely free from insoluble matter.

The residue obtained on the filter may consist of: (1) Water-soluble substances, such as chloride, sulphate, carbonate, silicate, or borate of the alkalis. (2) Mineral substances insoluble in water, viz. colouring matters and 'filling' and 'weighting' substances. (3) Organic substances, especially starch, dextrin, or gelatin (Carragheen mucilage).

(1) **Water-soluble substances.** The residue on the filter is washed with cold water so as not to dissolve any gelatin that may be present. Presence of silicate (if any) will have been noticed already in the determination of fatty matter when decomposing the soap by acid (*see* above under (a)). If the silica has not been estimated in the same portion in which the amount of fatty matter has been ascertained (provided no other water-insoluble substance be present), it can be determined at this stage by acidifying the filtrate with hydrochloric acid after the total alkali present in it has been determined by titration, and evaporating to dryness in the usual manner. The filtrate from the separated silica may be tested for boric acid. If boric acid be absent the amount of carbonate *plus* silicate can be calculated from the alkali found by titration, the silica having been found direct by weighing. If boric acid be present and the proportion of borate be required, the water-soluble portion is best divided into three parts. In one portion the carbon dioxide is estimated, in a second portion the silica, and in the third the total alkali is determined by titration.

Chlorides and sulphates are best determined in aliquot portions of the acid liquor, obtained after separating off the fatty matter as described in (a). It should be remembered that in that case nitric acid must be employed for decomposing the soap.

(2) The portion insoluble in water is ignited, so as to burn off organic substances, and the residue is weighed. The ash is examined qualitatively and quantitatively in the usual manner.

(3) **Organic substances.** The microscopical examination of the total residue insoluble in alcohol may furnish useful indications. Thus starch will be detected; the microscopical examination may be corroborated by testing with iodine. If the quantitative determination of starch be required the residue on the filter insoluble in alcohol is washed with cold water to remove water-soluble substances and dextrin, and boiled with dilute sulphuric acid, replacing the water as it boils away in order to convert the starch into glucose. The liquid is then neutralised with barium carbonate, filtered, and the amount of glucose estimated by titration with Fehling's solution in the usual manner. *Dextrin* has been washed out by cold water simultaneously with the soluble salts. The proportion of dextrin is estimated by precipitation with alcohol. This is done best in a small beaker, tared with a glass rod. The liquid is stirred vigorously, so that all the dextrin is made to adhere to the sides of the beaker. The aqueous liquid is then poured off, the dextrin washed with alcohol, and its amount determined by weighing the beaker after drying at 100°. *Gelatin* is dissolved by washing the alcohol-insoluble residue with hot water. The filtrate should be tested with tannic acid to corroborate the presence of gelatin.

For the determination of other substances occurring in soap such as *glycerol, sugar, carbolic acid, alcohol, colouring matters, etheral oils,* &c., *see* Lewkowitsch, Chem. Techn. iii. 294–296.

(2) SALTS OF THE ALKALINE EARTHS AND HEAVY METALS — WATER-INSOLUBLE SOAPS—METALLIC SOAPS.

A number of insoluble soaps of the individual fatty acids have been described in the section

Fatty acids (*see* Oils, Fixed, and fats). These soaps are prepared by double decomposition of the alkali soaps with aqueous solutions of salts of the alkaline earths or metals, or by heating the free fatty acids with the oxides or carbonates of the metals.

These soaps are employed in the arts for the most varied purposes, extensive use being made of their property of dissolving, to a considerable extent, in petroleum ether, naphtha, heavier petroleum hydrocarbons, coal-tar oils (carbolic acid), oil of turpentine, and fatty oils. Their solubility is increased by the presence of free fatty acids.

The most important soaps are—

Lead soaps (lead plaster) consisting chiefly of lead oleate.

Magnesium oleate, used in the process of dry-cleaning to prevent spontaneous ignition. **Aluminium soaps** enter into many compositions for waterproofing textile goods and papers, for preparing substitutes for leather, celluloid, india-rubber substitutes for insulating purposes, &c. Aluminium oleate is used especially as an 'oil thickener.' **Lead and manganese soaps** are used as 'driers' (*q.v.*) in the manufacture of boiled oils and varnishes. **Zinc, iron, nickel, cobalt, and chromium soaps** are employed in the manufacture of coloured varnishes, as also for waterproofing leather and canvas, and to some extent as 'driers.' **Copper and mercury soaps** serve in the production of anti-fouling preparations, especially in the manufacture of paints for ship bottoms.

In this class of soaps must be also included the *metallic rosinates*, chiefly used as 'driers' (*q.v.*).

In the analytical examination the water-insoluble soaps are decomposed by means of a suitable mineral acid (hydrochloric, nitric, sulphuric), when the fatty acids are obtained as an oily layer; or, if the salts be decomposed under ether (which in many cases is the most advisable course), in ethereal solution, and the metal passes into the acid solution. Both the fatty acids and the acid liquor are then examined in the usual manner. J. L.

SOAP-BARK and SOAP-ROOT. Soap-bark is the bark of a Chilean rosaceous tree, *Quillaja saponaria* (Mol.). The thin black dead bark has usually been almost or entirely removed from the commercial product, which consists mainly or exclusively of the heavy white layer of bast which glitters with crystals of calcium oxalate. This salt is mainly responsible for the large amount (13 p.c.) of ash present. The bark when shaken up with water yields a frothy solution, which is neutral in reaction, and is used in cleaning cloth when it is important to preserve the original colours. The emulsifying substance is *saponin* (a collective name for a group of glucosides), which is not toxic, but is accompanied by two poisons, sapotoxin and quillajic acid. Saponin is widely distributed in flowering plants, and is usually associated with toxic substances. Its presence is familiar in a number of caryophyllaceous plants belonging to the genera *Saponaria*, *Gypsophila*, *Dianthus*, *Lychnis*, *Silene*, and others, whose underground parts are known as '*soap-roots.*' The ordinary (red) soap-root is composed of underground stems and roots of the soap-wort, *Saponaria officinalis* (Linn.); the (white) soap-root of Hungary, Mediterranean countries, the Levant, and the East, is composed of the peeled roots of various species of *Gypsophila*.

SOAPSTONE *v.* Talc.

SOAP-WORT. *Saponaria officinalis v.* Soap-bark.

SOBREROL *v.* Terpenes.

SOD OIL *v.* Dégras.

SODA (NATIVE) *v.* Natron; Trona.

SODALITE. A rock-forming mineral of the composition $Na_4(AlCl)Al_2(SiO_4)_3$ and crystallising in the cubic system. Other members of this group of minerals are mentioned in the article Lapis-lazuli. It is white, grey, or bright blue in colour; sp.gr. 2·3; and occurs as a constituent of the igneous rock sodalite-syenite. At Litchfield in Maine, on the Ice River in Kootenay Co., British Columbia, and at Bancroft in Hastings Co., Ontario, large masses of sky blue to deep blue sodalite are found. At Bancroft it has been quarried in some quantity for use as an ornamental stone under the trade-names 'Princess Blue' and 'Alomite.' The material takes a good polish, and has somewhat the appearance of marble, but it is considerably harder (H.$=5\frac{1}{2}$) than this.

L. J. S.

SODA-NITRE *v.* Nitratine.

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